

CANADIAN JOURNAL OF RESEARCH

VOLUME 16

SEPTEMBER, 1938

NUMBER 9

CONTENTS

SEC. A.—PHYSICAL SCIENCES

	Page
The Heat Capacity of Bismuth from -80° to 120° C.— <i>H. L. Bronson and L. E. MacHallie</i> - - - - -	177
Production and Frequency Measurement of Currents Having Frequencies from 10 to 100 Cycles per Second— <i>A. L. Clark and L. Katz</i> - - - - -	183

SEC. B.—CHEMICAL SCIENCES

Persistence of the Liquid State of Aggregation above the Critical Temperature— <i>R. L. McIntosh and O. Maass</i> - - - - -	289
The Mercury Photosensitized Decomposition of Ethane. II. The Production of Hydrogen and the Mechanism of the Reaction— <i>E. W. R. Steacie and N. W. F. Phillips</i> - - - - -	303
The Mercury Photosensitized Decomposition of Ethane. III. The Reaction in the Presence of Added Deuterium— <i>E. W. R. Steacie, W. A. Alexander, and N. W. F. Phillips</i> - - - - -	314
Equilibria in Two-phase, Gas-liquid Hydrocarbon Systems. II. Methane and Pentane— <i>E. H. Boomer, C. A. Johnson, and A. G. A. Piercey</i> - - - - -	319
Equilibria in Two-phase, Gas-liquid Hydrocarbon Systems. III. Methane and Hexane— <i>E. H. Boomer and C. A. Johnson</i> - - - - -	328

NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA



Publications and Subscriptions

The Canadian Journal of Research is issued monthly in four sections, as follows:

- A. Physical Sciences
- B. Chemical Sciences
- C. Botanical Sciences
- D. Zoological Sciences

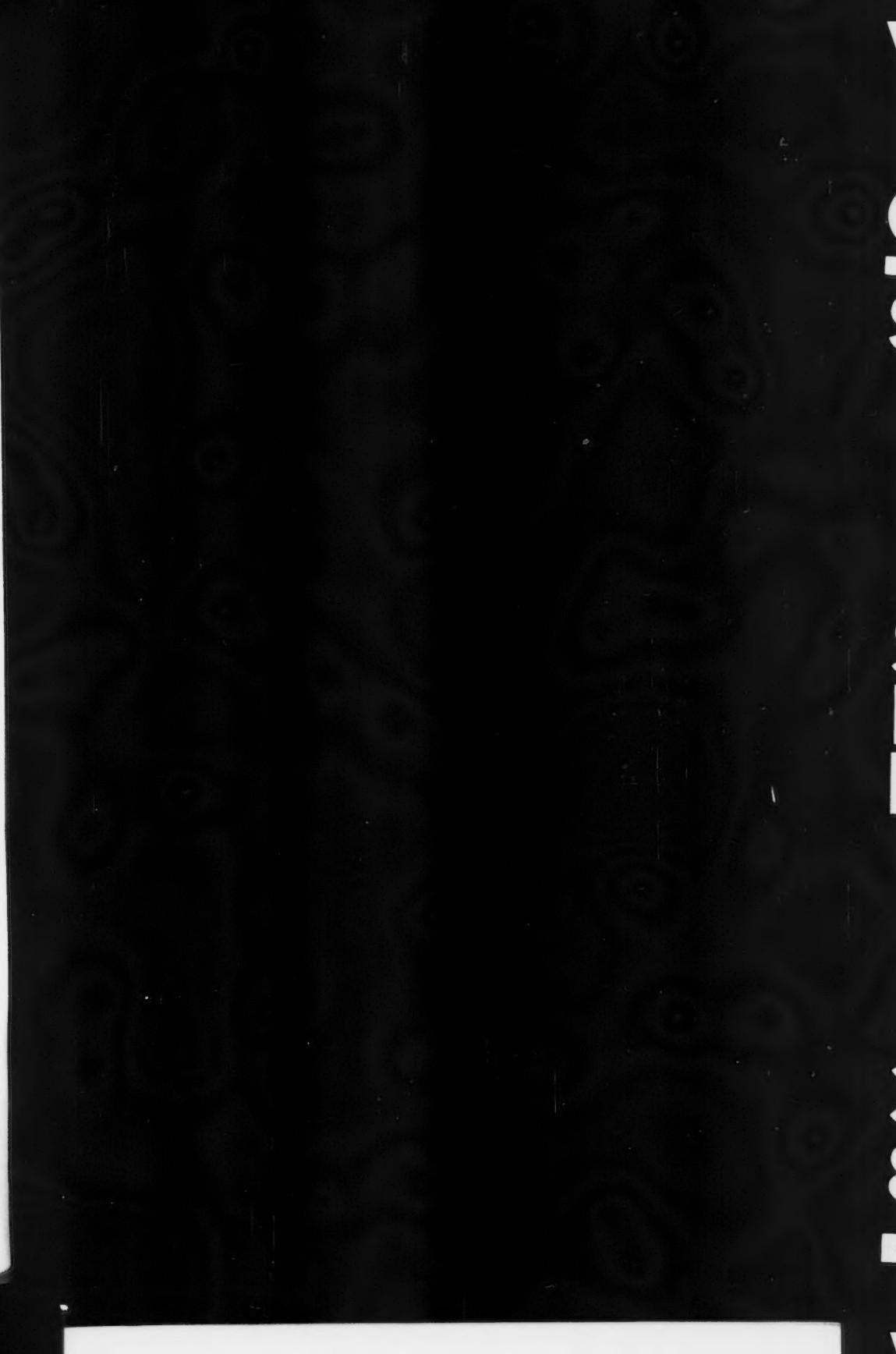
For the present, Sections A and B are issued under a single cover, as also are Sections C and D, with separate pagination of the four sections, to permit separate binding, if desired.

Subscription rates, postage paid to any part of the world, are as follows:

	<i>Annual</i>	<i>Single Copy</i>
A and B	\$ 2.50	\$ 0.25
C and D	2.50	0.25
Four sections, complete	4.00	—

The Canadian Journal of Research is published by the National Research Council of Canada under the authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. All correspondence should be addressed:

National Research Council, Ottawa, Canada.





Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 16, SEC. A.

SEPTEMBER, 1938

NUMBER 9

THE HEAT CAPACITY OF BISMUTH FROM -80° TO 120° C.¹

By H. L. BRONSON² AND L. E. MACHATTIE³

Abstract

The mean heat capacity of bismuth over 10° intervals has been determined from -80° to 120° C. by means of adiabatic electrical heating in a copper jacket. The maximum deviation of any individual point from a smooth curve is 0.1%, and the error in the absolute values obtained is considered to be not more than 0.1%. No discontinuities or irregularities were found; in fact, the experimental results are represented to within the limits of experimental error by the linear equation:

$$C_p = 0.1238_8 + 4.45 \times 10^{-3}t,$$

where t is the Centigrade temperature, and the units are joules per gram per degree. The equation:

$$C_p = \frac{1}{209.0} D\left(\frac{119}{T}\right) + 3.99_7 \times 10^{-3} T^{1.703}$$

was found to fit the mean experimental curve as closely as the graph could be read (0.02%). T is the absolute temperature and $D(119/T)$ the Debye function for C_v per mole. C_p is given in joules per gram per degree. A calculation of C_p from non-thermal data gives values about 3% low.

Introduction

This paper describes a continuation of the work of Bronson and Wilson (3). The same apparatus and method have been applied to the measurement of the heat capacity of bismuth.

As is well known, many of the properties of bismuth are peculiar. Besides being very diamagnetic it has a specific resistance higher than that of most if not all metals, and it expands on solidifying. Goetz and Jacobs (6) reported discontinuities or rapid changes in the coefficient of expansion of the crystal lattice spacing of bismuth. Gruneisen's law, then, might lead one to suspect similar peculiarities in the heat capacity. From this it would seem that the investigation of the heat capacity might be of considerable interest.

Preliminary Work

All the apparatus was re-calibrated and the thermal insulation was adjusted again as though the apparatus were being assembled for the first time. The aim was to keep temperature variations over the inside surface of the copper jacket within 0.01° C. However, these adjustments required much time, and there was no certainty that after the adjustments were made the thermal

¹ Manuscript received August 3, 1938.

Contribution from the Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada.

² Professor, Department of Physics, Dalhousie University.

³ Holder of MacGregor Teaching Fellowship in Physics, 1937-1938, Dalhousie University.

conditions would be sufficiently well reproduced following removal and replacement of the copper jacket, or with varying values of relative humidity. It was therefore decided to ascertain the magnitude of the error that would be introduced by large temperature differences in the jacket.

Determinations were made with the silver specimen used by Bronson and Wilson, current being supplied to the heating coils on the sides and bottom of the jacket but not to the top coil. This gave a temperature difference between the bottom and top of the jacket of 0.5°C . at 93°C . After the jacket had been brought to a steady temperature following a temperature rise, the platinum thermometer indicated a falling temperature for 20 min. owing to the redistribution of heat flow from the heating coil on the upper side of the jacket. Here, then, was an opportunity to so adjust the position of the platinum thermometer that it would indicate the mean temperature of the thermojunctions in the jacket, a point about which there had previously been some uncertainty. The thermometer was raised until it registered a steady temperature after a rise, and friction tape was wrapped around its stem to hold it in the new position. An X-ray photograph showed that this held the middle of the platinum coil within 1 mm. of the joint between the two halves of the jacket. Two measurements then made with the silver specimen at 77° and 88°C . showed the surprisingly small deviations of 0.06 and 0.09% respectively from the experimental values of Bronson and Wilson.

Since it was thus found that a much rougher approximation of temperature uniformity in the jacket was sufficient, adjustments were made to keep temperature variations within 0.05°C . before measurements were taken.

Measurements

Several series of determinations were made as described by Bronson and Wilson, the only difference being that the series taken with the calorimeter surrounded by solid carbon dioxide were extended to 40° and 80°C . instead of to 30° and 40°C .

As a check on these measurements with the copper jacket, several determinations near room temperature were made, the water bath and jacket employed by Bronson, Chisholm, and Dockerty (2) being used. These measurements were 0.07% higher than the mean of the others; this is considered quite satisfactory agreement. Although this apparatus is similar in principle, it should be emphasized that the differential thermocouples, the suspension wires and method of suspension, the size of the jacket cavity, and the thermal relation between the thermometer and the jacket thermocouple junctions are all physically different, and hence provide some assurance that no unsuspected blunder or large systematic error has crept in.

In all, 65 heat capacity determinations were made. The results were plotted on large-scale graph paper on which 2 mm. represented 1 in the fourth figure of the value of C_p . Mean experimental values for every 20° were determined by stretching a fine black wire over short sections of the graph and moving it until it appeared to be the best line through the points. This

was done several times. The averages of the values so obtained are given in Table I, Column II.

No indications of any discontinuity in the heat capacity curve or in its slope were found in the temperature range covered.

Empirical Equations

It was found that, within the limits of experimental error, a linear equation would represent the experimental results over the whole temperature range. The equation in terms of Centigrade temperature is:

$$C_p = 0.1238_3 + 4.45 \times 10^{-5}t, \quad (1)$$

where C_p is the number of joules per gram per degree.

Since, however, the experimental graph appears to be concave downwards from -80° to 0° C. and concave upwards from 0° to 120° C. (Table I, Column IV), an attempt was made to obtain a closer fit by use of an equation of the form $C_p = \frac{1}{M} D\left(\frac{\theta}{T}\right) + AT^n$, where M is the molecular weight, $D\left(\frac{\theta}{T}\right)$ is the Debye function for C_v per mole, and T is the absolute temperature.

TABLE I

I Temp., °C.	II Experimental graph	III Equation (1)	IV Difference II-III	V Equation (2)	VI Difference II-V
120	0.1292 ₈	0.1291 ₉	+ 0.0000 ₉	0.1292 ₈	0.0000 ₀
100	.1283 ₄	.1283 ₀	+ 0 ₄	.1283 ₂	+ 0 ₁
80	.1273 ₉	.1274 ₁	- 0 ₂	.1274 ₀	- 0 ₁
60	.1264 ₉	.1265 ₂	- 0 ₃	.1264 ₉	0 ₀
40	.1256 ₁	.1256 ₃	- 0 ₂	.1256 ₀	+ 0 ₁
20	.1247 ₂	.1247 ₄	- 0 ₂	.1247 ₃	- 0 ₁
0	.1238 ₅	.1238 ₅	0 ₀	.1238 ₆	- 0 ₁
-20	.1230 ₁	.1229 ₆	+ 0 ₅	.1229 ₉	+ 0 ₂
-40	.1221 ₀	.1220 ₇	+ 0 ₃	.1221 ₁	- 0 ₁
-60	.1212 ₀	.1211 ₈	+ 0 ₂	.1212 ₀	0 ₀
-80	.1202 ₅	.1202 ₉	- 0 ₄	.1202 ₄	+ 0 ₁

The constants θ , A , and n , in this equation were determined empirically as follows. By trial and error it was found possible to obtain a value of θ , the characteristic temperature, such that $C_p - \frac{1}{M} D\left(\frac{\theta}{T}\right)$ could be accurately represented by a term of the form AT^n . This means that a plot of $C_p - \frac{1}{M} D\left(\frac{\theta}{T}\right)$ against T on logarithmic paper would yield a straight line from which A and n could be determined. The value so found was 119 to the nearest integer. This is considerably greater than the value 107 calculated from previous low temperature, heat capacity measurements (8), but is in tolerably good agreement with the value 116 calculated from elastic constants (see note in Table II). Too much significance should not be

attached to the value 119, for this value obviously depends on the form of the term or terms chosen to represent $C_p - \frac{1}{M} D \left(\frac{\theta}{T} \right)$. The equation obtained is:

$$C_p = \frac{1}{209.0} D \left(\frac{119}{T} \right) + 3.997 \times 10^{-7} T^{1.703} \quad (2)$$

in joules per gram per degree. Values given by this equation and the differences between these and the experimental results are given in Table I, Columns V and VI, from which it will be seen that the equation represents the experimental results as accurately as these can be read from the graph. Moreover its slope agrees well with that of the experimental graph at the two extremities of the range. This agreement indicates that the equation can probably be extrapolated with safety for some distance. This cannot be done with the linear equation.

In connection with Equation (2) it is well to draw attention to the fact that at 120° C. a change of 1 in the fourth figure of the exponent of T changes the fifth figure of C_p by 6, and a change of 1 in the third figure of A changes the fifth figure of C_p by 3. However, a small change in one of these quantities can be practically compensated for by a change in the other. Thus the accuracy to which each must be expressed in order that a certain accuracy in the calculated value of C_p (Table I, Column V) may be obtained is greater than the accuracy of determination of their absolute values. As for the characteristic temperature, a change of 1 in it just produces a detectable curve in the logarithmic plot.

Since the relative accuracy of values of the heat capacity at different temperatures is greater than their absolute accuracy, the agreement of Equation (2) with the experimental results within narrower limits than the probable experimental error would seem to be more than coincidence and may have theoretical significance.

Sources of Error

An analysis of the batch of bismuth from which the specimen was made has been supplied by the Consolidated Mining and Smelting Company of Canada; it showed the following impurities: Pb, less than 0.002% (by spectrograph); S, 0.020%; Cu, 0.0022%; As, less than 0.00005%.

The bismuth equivalent of the specimen was calculated in the usual way (3). The equivalent of all non-bismuth components amounted to 0.63% of the total bismuth equivalent, and of this, about half was that of metals whose specific heat is known to within 1%.

In most of the determinations in which the calorimeter was surrounded by dry ice there was a downward temperature drift when the jacket-to-specimen thermocouple indicated no temperature difference. The average of the rates of drift before and after a measurement was assumed for the heating period and a correction applied. The correction for the greatest drift was 0.25%. There are reasons for believing that the drift was not due to sublimation of

frost or evaporation of moisture on the specimen, but its cause has not been definitely ascertained. Satisfactory evidence, however, that the drift has not introduced any appreciable systematic error in the determinations is found in the fact that where the series of measurements taken with the calorimeter surrounded by solid carbon dioxide overlap those taken with room temperature surroundings no difference is noticeable in the scattering of the individual points of the two series about the mean. This overlapping extended from 10° to 80° C.

The systematic error in the estimation of which there is more uncertainty than in any other lies in the heat transfer between jacket and specimen during the heating period. Transfer will take place if the lag between the mean temperature of the jacket thermocouple junctions and the jacket surface is not equal to the lag between the mean temperatures of the junctions in the specimen and its surface. This error cannot be detected by changing the rate of heating or the temperature interval of a determination. Seemingly, the only possible way to detect the change is to use a specimen in a container whose heat capacity can be determined when full and when empty, thus using it as a transfer instrument. As stated by Bronson and Wilson, it is considered unlikely that this error would be as large as that due to a constant temperature difference of 0.01° C., which a rough calculation shows would cause an error of 0.06%.

Of the factors in the expression for the heat capacity, it is estimated that the temperature interval has the largest probable error. It is unlikely that this error is as great as 0.05%.

The maximum deviation of any point from a smooth curve is 0.1%, and the average deviation, 0.03%.

TABLE II

Temperature, °C.	30	75
θ	116	116
$\frac{1}{M} \left(D \frac{\theta}{T} \right)$	0.1184 _s	0.1186 _s
$10^3\alpha$	3.96	4.33
ρ	9.79	9.79
$10^{12}\beta$	2.98	3.05
$\frac{\alpha^2 T}{\rho\beta}$	0.0016 _s	0.0021 _s
c_t	0.0015 _s	0.0017 _s
C_p , calc.	0.1216	0.1226
C_p , obs.	0.1252	0.1272
Difference, %	2.9	3.6

NOTE—Sources of data:

θ —Calculation of Debye (5) but using recent values of constants.

α —I.C.T. (7) (Fizeau).

ρ —Measured.

β —I.C.T. (7) (Bridgman).

c_t —Calculated from formulas given in Reference (9), on the assumption of one free electron per atom.

needed in the expression for the heat capacity or that the assumption of harmonic oscillations in the crystal lattice is not valid for bismuth at ordinary temperatures.

This discrepancy has been noted by Carpenter and Harle (4) and attributed to anharmonic oscillations.

Results of Previous Observers

A comparison of values obtained in the present work with those in the International Critical Tables and some of the more recent work is given in Table III. The equation given in the I.C.T. as representing "best" values is:

$$C_p = 25.4 + 0.0116t \quad (25^\circ \text{ to } 200^\circ \text{ C.})$$

where C_p is in joules per gram-atom. In the same units Equation (1) becomes:

$$C_p = 25.88 + 0.00930t$$

TABLE III

Source	Date	Tempera-ture, °C.	Value	Accuracy claimed	Writers' value	Difference
I.C.T. (7) "best" values		30	25.7 ₆	"Rarely better than 1%"	26.16	1.5% low
		70	26.2 ₂		26.53	1.2% low
		120	26.8 ₀		27.00	0.74% low
Anderson (1)	1930	-60	5.94	1%	6.050	1.8% low
		-20	6.02		6.141	2.0% low
		20	6.09		6.227	2.2% low
Carpenter and Harle (4)	1932	33	6.18	1.3%	6.255	1.2% low
		99.6	6.35		6.405	0.86% low
Thomas and Davies (10)	1937	20	.0308 _s		.02979	3.7% high

Acknowledgment

The writers wish to express their indebtedness to Dr. C. H. Wright and to the Research Laboratory of the Consolidated Mining and Smelting Company of Canada who kindly presented the bismuth specimen and furnished the chemical analysis.

References

1. ANDERSON, C. T. J. Am. Chem. Soc. 52 : 2720-2723. 1930.
2. BRONSON, H. L., CHISHOLM, H. M. and DOCKERTY, S. M. Can. J. Research, 8 : 282-303. 1933.
3. BRONSON, H. L. and WILSON, A. J. C. Can. J. Research, A, 14 : 181-193. 1936.
4. CARPENTER, L. G. and HARLE, T. F. Proc. Roy. Soc. 136 : 243-250. 1932.
5. DEBYE, P. Ann. Physik, 39 : 789-839. 1912.
6. GOETZ, A. and JACOBS, R. B. Phys. Rev. 51 : 159-164. 1937.
7. INTERNATIONAL CRITICAL TABLES. McGraw-Hill Book Company, New York. 1933.
8. KEESEOM, W. H. and VAN DEN ENDE, J. N. Proc. Acad. Sci. Amsterdam, 34: 210-211. 1931.
9. STONER, E. C. Phil. Mag. 21 : 145-160. 1936.
10. THOMAS, W. J. and DAVIES, R. M. Phil. Mag. 24 : 713-744. 1937.

**PRODUCTION AND FREQUENCY MEASUREMENT OF CURRENTS
HAVING FREQUENCIES FROM 10 TO 100 CYCLES
PER SECOND¹**

By A. L. CLARK² AND L. KATZ³

Abstract

A low frequency dynatron oscillator with a range of 10 to 100 cycles per sec. and a power output of 10 watts is described. The frequency is measured by taking photographs, at intervals of one second, of two pointers on a small synchronous motor powered by the current whose frequency is to be measured. The stability of the oscillations and the accuracy of the frequency measurements are such that frequencies may be maintained and measured to 1 part in 30,000, over a period of several hours.

It is sometimes found necessary, in the laboratory, to have a supply of alternating current of low and variable frequency. The need for such a current arose in connection with the design of an apparatus for the measurement of the ratio of the specific heats of gases.

Production and measurement of high frequency currents have been satisfactorily accomplished with the design of crystal oscillators, coupled with multi-vibrators and high frequency synchronous motors, which, though excellent in performance, are costly to build and offer only discrete submultiples of the fundamental period of the crystal. This paper describes an oscillator that is comparatively inexpensive to build and that has a wide range of frequency output and exceptional stability. An accurate means of measuring the frequency is also described.

The oscillator with three stages of amplification is shown in Fig. 1. It is of the dynatron type, using the negative resistance of a 24-A tube.*

For stability the dynatron is powered entirely by batteries; however, any steady supply should prove satisfactory. The correct plate and screen-grid voltages to be used depend on the individual tube characteristics, and are found experimentally. The particular tube used was found to operate best with 115 volts on the screen and 32.4 volts on the plate. Under these conditions it has a screen emission of 11.5 ma. To minimize the effect of temperature changes, an air-core inductance is used since the permeability of an iron core changes with temperature, and this would affect the frequency. L , Fig. 1, is an air-core inductance and C_1 is a mica condenser.

¹ Manuscript received July 21, 1938.

Contribution from the Department of Physics, Queen's University, Kingston, Ontario, Canada.

² *Dean of the Faculty of Applied Science, Queen's University.*

³ *Holder of a bursary under the National Research Council of Canada.*

* *It has been recently found that the negative-transconductance between the third and second grids of an RCA-57 tube is better suited for this purpose.*

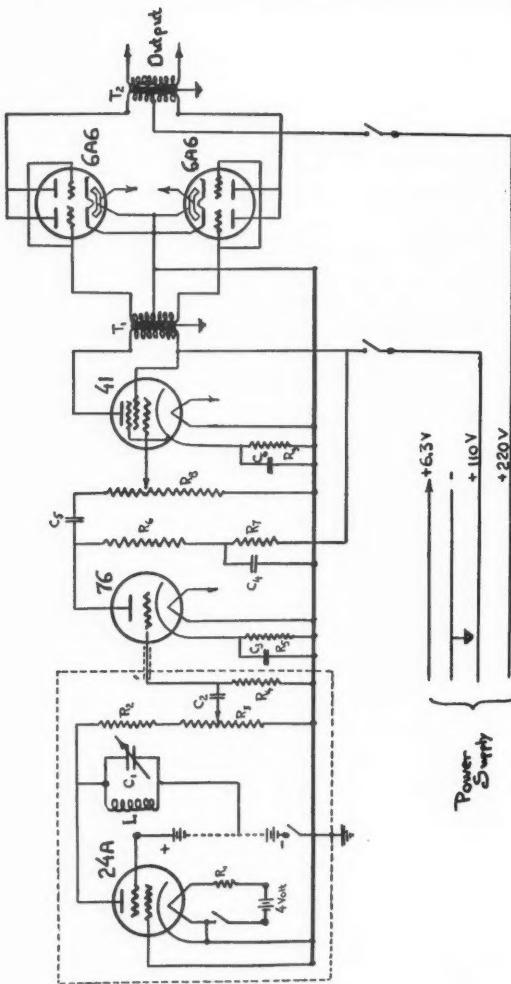


FIG. 1. Dynatron oscillator.

$L = 10 \text{ henry}, 130 \text{ ohm, air core}$	$R_4 = 50,000 \text{ ohms}$
$C_1 = 0 \text{ to } 10 \mu\text{f} \text{ variable condenser}$	$R_5 = 7,000 \text{ ohms}$
$C_2 \text{ and } C_3 = 0.1 \mu\text{f}, 250 \text{ volt}$	$R_6 = 0.1 \text{ megohm}$
$C_4 = 10 \mu\text{f}, 25 \text{ volt}$	$R_7 = 25,000 \text{ ohms}$
$C_5 = 2 \mu\text{f}, 250 \text{ volt}$	$R_9 = 670 \text{ ohms}$
$C_6 = 50 \mu\text{f}, 25 \text{ volt}$	$\frac{P}{T_1 S} = 11,000 \text{ ohms}$
$R_1 = 0.95 \text{ ohm}$	$T_2 \frac{S}{2} = 690 \text{ ohms}$
$R_2 = 1 \text{ megohm}$	$T_2 \frac{P}{S} = 5,000 \text{ ohms}$
$R_3 \text{ and } R_8 = 0.5 \text{ megohm}$	$T_2 \frac{P}{S} = 5,000 \text{ ohms}$

where L , C , and R are respectively the inductance, capacity, and resistance of the tank circuit, and $-R_p$ is the negative resistance of the tube, which is measured experimentally.

If C in Equations (1) and (2) is eliminated—

$$\frac{L^2}{R} \cong -\frac{(-R_p)}{4\pi^2 f^2}. \quad (3)$$

The greater part of the tank circuit resistance is due to the inductance; thus Equation (3) actually gives the proper ratio between L and R for the coil, in terms of the tube negative resistance and frequency desired. From this ratio it is possible to determine the most efficient type of inductance to be used, and then the correct capacity is calculated by means of either Equation (1) or (2). By use of these calculations for a frequency of 10 to 100 cycles, L was fixed at 10 henrys, R at 130 ohms and C was made variable up to 10 μ f.

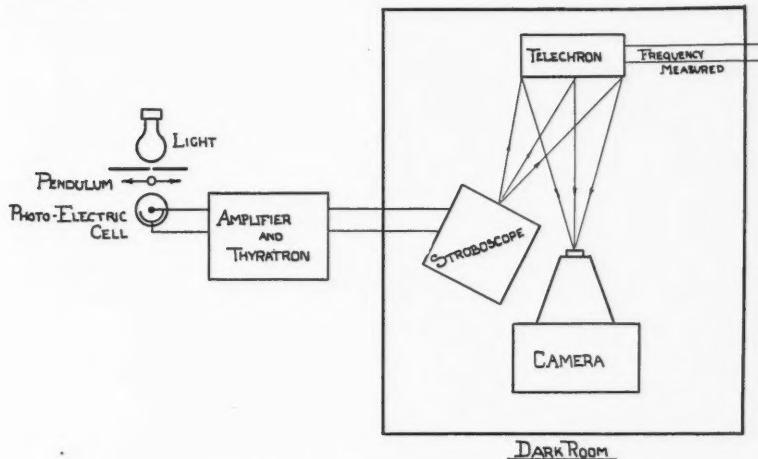


FIG. 2. Method of measuring the frequency.

The variable 10 μ f. condenser was constructed as follows. Four sets of 10 mica condensers of capacities of 1 μ f., 0.1 μ f., 0.01 μ f., and 0.001 μ f. were used. Each set was placed in a semicircle and a rotating dial allowed to connect the individual condensers, one at a time, in parallel. The four dials were connected together. With this arrangement it is possible to obtain any capacity between 0.001 and 10 μ f. Finer adjustments are made by placing an ordinary radio condenser in parallel with this set-up.

To measure the frequency, high speed photographs are taken, at intervals of one second, of two pointers on a small synchronous motor powered by the oscillator. The frequency is then determined from the positions of the pointers on these photographs. The method is illustrated in Fig. 2. The

pendulum of an accurate clock interrupts a light beam falling on a photoelectric cell: this gives, at intervals of one second, impulses which when amplified are used to actuate a thyratron. The thyratron in turn discharges a condenser through the primary of a spark coil, and provides a control spark for flashing a stroboscope.* Photographs of the pointers on the synchronous motor are then taken by the light of the stroboscope flash, and the frequency is determined.

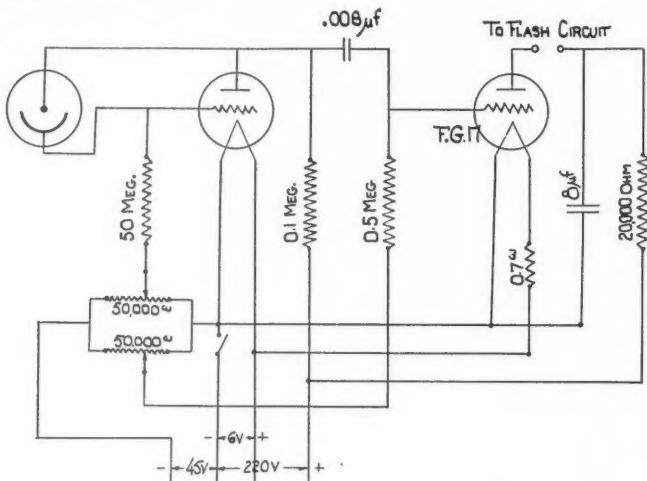


FIG. 3. Wiring diagram of photoelectric cell with amplifier and thyratron. Type VB Westinghouse photoelectric cell.

The actual wiring diagram of the photoelectric cell and thyratron and of the stroboscope are shown in Figs. 3 and 4, respectively. The mechanical details of the clock mechanism embodying the light system and photoelectric cell are shown in Fig. 5.

The two pointers on the synchronous motor were so geared that one makes one revolution in 50 cycles while the other makes one revolution per cycle. The dial, which is 5 in. in diameter, is divided into 100 equal parts; consequently, the frequency may be estimated to 1/1000 part of a cycle.

The photographs are taken on a piece of standard 35 mm. movie film wrapped around a drum. By pressing a key the drum is caused to rotate through an angle of 24 degrees (15 picture frames per circumference) with a slight lag behind the flashing of the stroboscope. The drum was rotated by means of an electromagnet and a spacer mechanism from an old typewriter. A small 60 tooth gear, attached to the "second" hand spindle of the clock, gave impulses for energizing the magnet. The angle of the lag mentioned is controlled by the position of the gear-wheel on the "second" hand spindle.

* The argon filled lamp and design of the stroboscope were kindly supplied by Mr. H. E. Edgerton of the Massachusetts Institute of Technology.

The stroboscope, synchronous motor, and camera (fitted with an f 8 lens) were placed in a dark room, and the camera lens was opened. By depressing two keys (No. 1 in the stroboscope circuit, to control the flashing of the stroboscope, and No. 2 in the camera mechanism to control the rotation of

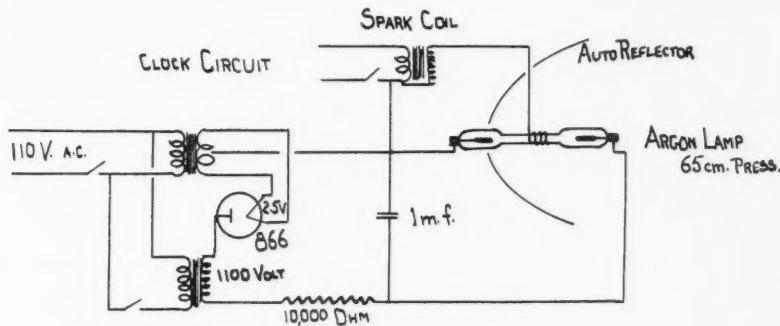


FIG. 4. *Stroboscope circuit.*

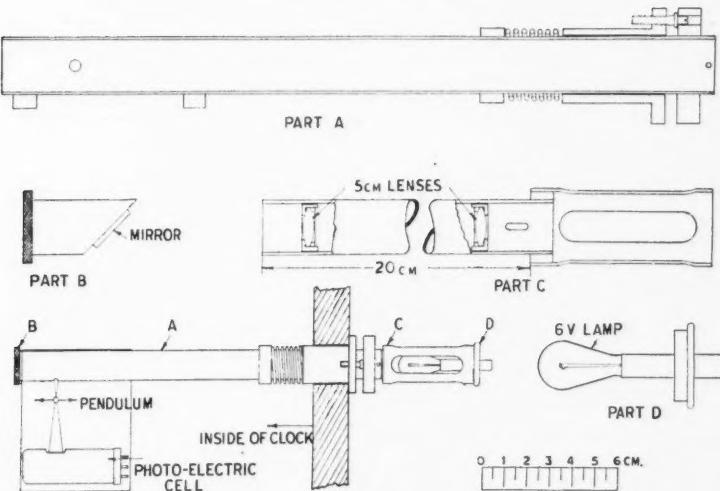


FIG. 5. *Clock mechanism.*

the drum) the stroboscope was caused to flash, and this was followed slightly later by a rotation of the drum. Key No. 2 is released and the next nine consecutive flashes are allowed to fall on the second frame of the film; the eleventh flash is then recorded on the third frame by pressing key No. 2 immediately after the ninth flash. Thus the difference in the readings of the telechron pointers in the first and third frames plus some whole number

of revolutions* gives the number of cycles over a period of 10 sec. This process could be repeated for any number of flashes. Since the two halves of the pendulum swing may not be equal in length, it is important that the duration of a frequency measurement be an even number of seconds (corresponding to equal numbers of left- and right-hand halves of the pendulum swing).

The synchronous motor, of a type generally used in electric clocks†, was placed directly across the oscillator output in parallel with the load. No variation in the frequency could be detected with changes in the load.

Table I summarizes the results of a test to determine how the frequency output of the oscillator varied from second to second.

The first column shows the readings of the pointers, to the estimated third decimal place, as recorded on the film. The second gives the difference between consecutive readings in the first column. It will be noticed that the frequencies, as shown, agree only in alternate pairs. This is because the photoelectric cell is not exactly in the centre of the pendulum swing. However, no error is introduced if the average frequency over one complete pendulum swing or two seconds, is taken, as shown in Column 3. It is seen that the maximum deviation from the mean value is only 1 part in 27,000.

To check the variation of the frequency over a somewhat longer period of time, say 15 min., the test summarized in Table II was made. Here the frequency was measured at five-minute intervals, the average over six consecutive seconds being taken, to give greater

TABLE I
VARIATION IN FREQUENCY FROM SECOND TO SECOND

Photograph reading	Difference	Average per pair
23.505	27.485	
0.990	27.494	27.489
27.484	27.482	
5.966	27.494	27.488
33.460	27.483	
10.940	27.497	27.490
38.440	27.480	
15.920	27.497	27.488
43.417	27.482	
20.899	27.497	27.489
48.396	27.480	
25.876	27.498	27.489
3.374		
Total average		27.489

TABLE II
VARIATION IN FREQUENCY OVER A PERIOD OF 15 MIN.

Time, min.	0	5	10	15	Mean
Average frequency over 6 sec.	27.421	27.421	27.421 _b	27.422	27.421 _a

* The number of revolutions to be added is obtained from an estimate of the frequency by recording two consecutive flashes.

† Canadian General Electric Company, Telechron motor C2: 6 watts, 110 volts, 30 cycles.

weight to the third decimal place. The frequency varied less than 1 part in 30,000, or 1/1000 of a cycle.

As may be seen from the results in Table III, the oscillator shows equally good characteristics over a much longer period of time. On the basis of the average frequency for a 10 sec. period, the output varied 1 part in 270,000 in a run of $5\frac{1}{2}$ hr.

TABLE III
VARIATION OF FREQUENCY OVER A PERIOD OF $5\frac{1}{2}$ HR.

Time, hr.	0	5	6	10.5	Mean
Average frequency over 10 sec. Oscillator started		27.3923	27.3924	27.3924	27.3924

The oscillator and frequency measuring device mutually check each other; thus if one or the other were not functioning properly, results as consistent as those shown in the tables could not be obtained. Table I indicates, to within the accuracy of frequency measurement, that the variation in the period of a pendulum oscillation from second to second is not large enough to affect the results appreciably. The *absolute* value of the frequency depends, of course, on the rate of the clock. This was checked against radio time signals and was found to be constant to within 3 sec. in 24 hr. or 1 part in 90,000.

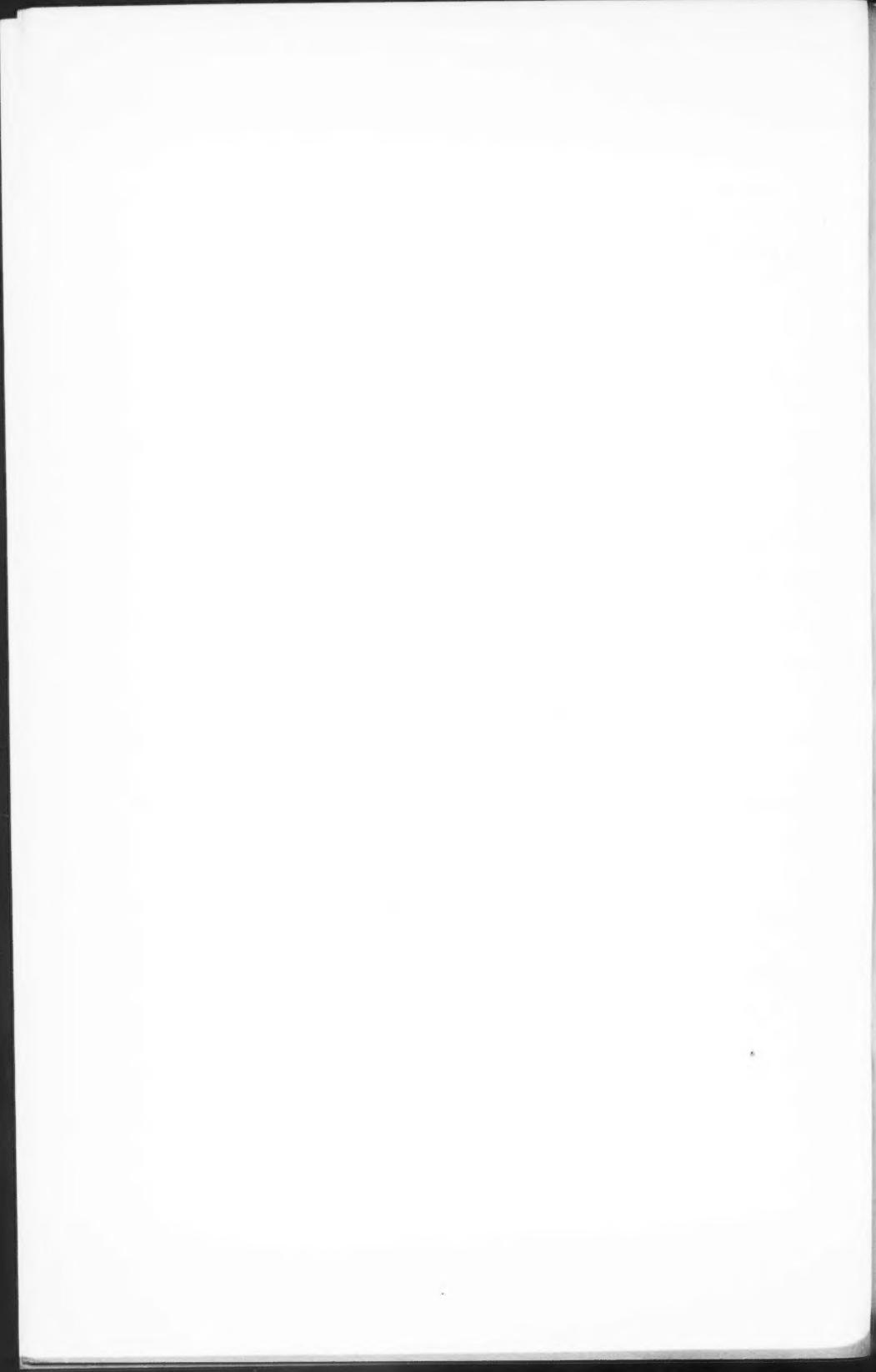
The entire equipment has been found to be very flexible and reliable in operation. The output is large enough to drive the telechron and leave enough power for many purposes. The ease with which the frequency may be maintained at any desired value has been most satisfactory.

Acknowledgments

The authors wish to acknowledge valuable suggestions made by Dr. W. A. Garrison of the Bell Telephone Laboratories and by Mr. K. A. MacKinnon of the Canadian Broadcasting Corporation.

References

- HUND, A. High frequency measurements. McGraw-Hill Book Company, New York. 1933.



Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 16, SEC. B.

SEPTEMBER, 1938

NUMBER 9

PERSISTENCE OF THE LIQUID STATE OF AGGREGATION ABOVE THE CRITICAL TEMPERATURE¹

BY R. L. MCINTOSH² AND O. MAASS³

Abstract

The data obtained by Maass and Geddes (7) on the properties of ethylene in the critical-temperature-critical-pressure region have been substantiated although it was shown that a small correction had to be applied to their absolute values of density. It was shown that at the critical density of ethylene the difference between the densities of the medium below and above the point at which the meniscus disappeared was a maximum. The conclusion of Mayer and Harrison (made in their recent papers on statistical mechanics of condensing systems (6, 10)) that, at a temperature just above that at which the meniscus disappeared, the pressure of the system remains constant over a considerable variation of mass per volume, has been corroborated. The effect of the presence of small measured quantities of air has been examined. The phenomena observed are explained on the basis that there is a difference between the gaseous and liquid states of aggregation with a structure assigned to the latter.

Introduction

In recent years, investigations (4, 7, 8, 9, 12, 13, 14, 17, 18, 19) of the properties of liquid-gas systems in the critical temperature region have been carried out in this laboratory. It was shown that the liquid state of aggregation can persist above the temperature* at which the visible meniscus disappears.

The present paper is a continuation of the study begun by Maass and Geddes (7) on the density of ethylene. Their experimental arrangement was such that any two of the factors, pressure, temperature, and density, could be varied, while the other was held constant. Time lags in the establishment of equilibrium densities could best be explained on the assumption of a dynamic structure in the liquid state. Measurements made at constant volume showed a persistence of a heterogeneous system until the temperature was approximately four degrees above the critical, while vapor pressure measurements showed the heterogeneous and homogeneous systems to have the same pressure within the limits of experimental accuracy. Isothermal compression and expansion were found to destroy the heterogeneity, and temperature fluctuations produced the same effect. The last two observations limit the kinds of mechanical stirring that may be employed in the

¹ Manuscript received July 27, 1938.

Contribution from the Division of Physical Chemistry, McGill University, Montreal, Canada, with financial assistance from the National Research Council of Canada.

² Holder of a bursary under the National Research Council of Canada.

³ Macdonald Professor of Physical Chemistry, McGill University.

* For convenience the authors refer to this temperature as the critical temperature.

investigation of critical temperature phenomena. Mechanical stirring that does not cause local heating and cooling, or expansion and compression, does not influence the phenomena observed, either in kind or in rate of attainment of equilibrium.

The present paper shows the main features of the investigation of Maass and Geddes to be reproducible. Further evidence of the persistence of the liquid state above the classical critical temperature has been obtained with pure ethylene and with ethylene-air mixtures.

Experimental Procedure

Density, Pressure, Temperature Measurements, etc.

The experimental arrangement employed for the measurement and control of pressure, temperature, and density was developed by Maass and Geddes (7) and described by them in a recent paper that must be consulted for the appreciation of the experimental method.

Purity of Ethylene Samples

The procedure followed by Maass and Geddes for the purification of the ethylene was to distil a large volume of ethylene of 99.9% purity three times, initial and final fractions being discarded. Two samples prepared by the above-mentioned authors in this way gave identical results.

For the investigation described below, a sample was prepared in this manner and compared with others that had been distilled through a Podbielniak column. All the samples behaved in an identical manner. Particular precautions were taken to ensure the absence of air due to slight leaks in stop-cocks. Before being filled, the apparatus was tested for long periods by means of a McLeod gauge.

Air-ethylene Systems

The air-ethylene samples were introduced into the apparatus as follows. Ethylene was prepared and inserted in the manner described previously (7). The stopcock in the lead to the bomb containing the ethylene was then closed, and the filling system evacuated and flushed with dry air several times. The cock in the lead from a small storage flask containing the air (the volume of which was accurately known) was opened, and the pressure read on the manometer. The cock in the bomb lead was then slowly opened, and air admitted until the desired pressure change was indicated on the manometer. The cock was then closed, and the bomb sealed off in the usual manner.

Critical Temperature of Air-ethylene Systems

It was thought possible that the temperature of disappearance of the visible meniscus might serve as a criterion of the purity of an ethylene sample. The data obtained are given in Table I.

It is seen that the critical temperature cannot be used as a test for the presence of small amounts of an inert gas. The best and quickest test for purity was found in the independence of the density of the liquid phase of the ethylene with changing ratios of liquid to vapor at 9.00° C.

TABLE I

Sample No.	1	2	3	4	5	6
Purity	100% C ₂ H ₄	Unknown air content	100% C ₂ H ₄	0.93% air	0.55% air	100% C ₂ H ₄
T _c , °C.	9.50	9.50	9.50	9.49	9.50	9.50

Experimental Results

The unusual nature and interest of the results of Maass and Geddes made the question of reproducibility an essential part of any subsequent work. The determination of typical isobars and isochores of the system ethylene was therefore repeated, particular attention being focused on the duration of time lags and the shapes of the curves.

In the course of the first experiments carried out with this object in view some air was inadvertently introduced into a sample of ethylene. The peculiarities of this system were such that it was deemed important to undertake an investigation of air-ethylene mixtures as soon as the limits of reproducibility had been determined.

Three typical isobars of samples of ethylene of satisfactory purity are given in Fig. 1. The isobars are identical in shape with those obtained by

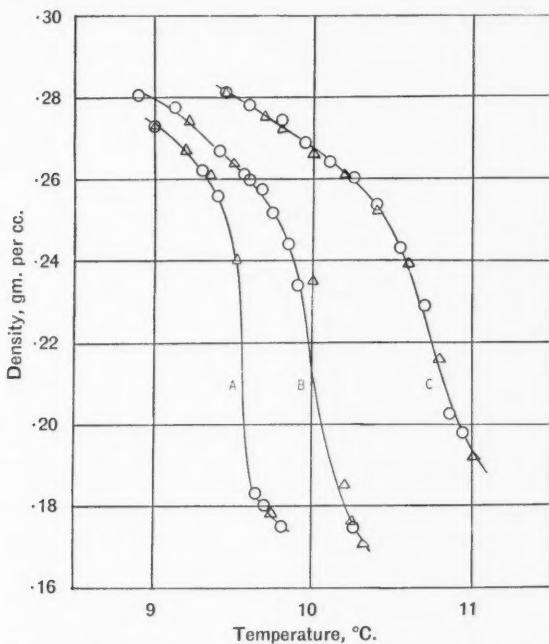


FIG. 1. Isobars of pure ethylene. A, 50.10; B, 50.54; C, 51.44 atm. Triangles denote Geddes' and Maass' values less 0.010 gm. per cc.

Geddes and Maass but show a difference of 0.0100 gm./cc. in the absolute value of the density all along the curves. This is very clearly illustrated by the good agreement between the triangular points (which are the values obtained by Geddes and Maass minus a constant factor of 0.0100 gm./cc.) and the curves, which are observed values. The cause of the discrepancy can be suggested and the present values are for several reasons believed correct. It is at once apparent that the carbon dioxide pressure cannot be the cause of the divergence, for the liquid density at 9.00° C., under the vapor pressure of the ethylene alone, and obtained by keeping the centre U-tube frozen, differs by the same factor of 0.0100 gm./cc. from the values of Geddes and Maass. The most likely source of error is therefore the calibration of the glass float by Geddes and Maass. The volume constant in the present work was reproducible to 3 parts in 800, the mean of a series being of course more accurate. Moreover, duplication with an entirely new apparatus, including a new spiral and new float, gave density values agreeing with each other

to 8 parts in 1000 on absolute values.

Although two samples of gas were used in the work of Geddes and Maass, none of their work was repeated by them with a different experimental unit; in this investigation work was repeated with a different unit. Table II shows the reproducibility of the liquid phase density at 9.00° C., where values of the density for different liquid-vapor ratios are given, as well as a check obtained with a new experimental unit. Consequently, it may be reasonable to assume that the absolute values of the data presented here are more nearly correct, and that although no change is indicated in the relative density measurements reported by Geddes and Maass, and in the conclusions drawn therefrom, nevertheless, their

TABLE II
DENSITIES OF ETHYLENE LIQUID AT 9.00° C.
FOR VARIOUS FILLINGS

Sample No.	Average density	Density of liquid
1	0.2161	0.2455
	.2334	.2460
	.2301	.2460
3	.2153	.2450
	.2210	.2450
	.2253	.2455
6	.2127	.2443

Densities of samples 1 and 2 were measured by means of one experimental set-up, the density of sample 3 by an entirely new set-up including new spiral and float. Samples 3 and 6 were put through the Podbielniak column. Absolute accuracy of density measurements are better than 1%. Relative accuracy of density measurements, 0.2%.

values should be corrected. This has been done in the pressure-temperature curves at constant volume given below.

PRESSURE-TEMPERATURE CURVES OF ETHYLENE

Various pressure-temperature curves of pure ethylene have been evaluated from the corrected isobars of Geddes and Maass for several densities. These are all excellent straight lines as Fig. 7 shows, and therefore follow the behavior predicted by Ramsay and Young for such isochores. The slopes have been used to test Mills' formula (11) that $\left(\frac{\delta p}{\delta T}\right)_V = \frac{2R}{V_e}$, where R has its usual

significance, and V_c is the critical molar volume. The calculated value of $2R/V_c$ for ethylene is 1.26 atm. per degree, while the corrected density values of Geddes and Maass' data give 1.21 atm. per degree as compared to 1.16 atm. per degree if Geddes' and Maass' uncorrected absolute values are used.

Reproducibility of Time Lags

The degree of agreement of the time lags is all that may reasonably be expected from the experimental method. Very small differences in absolute temperatures cause large changes in density, especially at those positions of the isobars where time lags are most sensitive. Moreover, the correction that must be applied for the changing mercury level involves a personal error. This is due to the fact that the temperature of the carbon dioxide has to be adjusted continuously in such a way that the proper temperature change is achieved at the desired time interval. Since the effect of pressure upon time lags and density is marked, slight differences in pressure cause divergences in the time required for equilibrium. The correct order of magnitude is therefore all that should be expected along the isobars, while much better agreement should be obtained in constant volume determinations where the U-tube is kept frozen. The results are given in Table III. In accordance with the practice initiated by Geddes and Maass, the results

TABLE III
TIME LAGS ALONG ISOBARS

Maximum time lags observed on heating +0.20° C., pressures being kept constant

Pressure, atm.	Geddes and Maass		McIntosh and Maass		
	Pure ethylene $t_{1/2}$, min.	Pure ethylene $t_{1/2}$, min.	0.93% air $t_{1/2}$, min.	0.55% air $t_{1/2}$, min.	
50.54	12	12	—	—	
51.44	7.5	5	6.5	4	

*Time lags observed on cooling so as to produce specified density changes (in pure ethylene)
pressures being kept constant at 50.54 atm.*

Geddes and Maass		McIntosh and Maass	
Density change	$t_{1/2}$, min.	Density change	$t_{1/2}$, min.
0.262 to 0.245	2	0.265 to 0.254	2.8
0.240 to 0.205	8	0.245 to 0.210	7

for the isobars are expressed in terms of the time required for the density change to reach the halfway mark, called the time to half value. The agreement is good.

In Table IV the times required for the establishment of equilibrium are given for isochore runs.

TABLE IV
TIME LAGS OF ISOCHORES*

	Pure ethylene		0.93% air	0.55% air
	Sample No. 3	Sample No. 6		
Temp. change, °C.	9.20 to 9.50	9.30 to 9.50	9.30 to 9.55	9.30 to 9.55
Density change	0.2354 to 0.2256	0.2325 to 0.2241	0.2544 to 0.2517	0.2469 to 0.2386
Time to equilibrium, min.	23	23	3	3
Temp. change, °C.	9.70 to 9.90	9.80 to 10.50	10.30 to 11.50	9.80 to 16.30
Density change	0.2094 to 0.2073	0.2175 to 0.2136	0.2175 to 0.2136	0.2346 to 0.2277
Time to equilibrium, min.	20	19	3	3

* Geddes and Maass—approximately 20 min. in all cases.

NOTE.—Cooling time lags of air-ethylene isochores are of same duration as the heating, i.e., 3 min.

For purposes of a comparison to be discussed later, the time lags for ethylene-air mixtures are included in Tables III and IV.

The time lag phenomenon first observed by Geddes and Maass, although not comprehensively reinvestigated, is shown to be reproducible within the limits of experimental error.

One Component System

The liquid and vapor densities at 9.50° C. were determined as functions of the mass per volume ratio in the following manner. The mercury level was adjusted so that the liquid or vapor phases, as the case might be, totally surrounded the float. The equilibrium density at 9.50° C. was then determined, as was the position of disappearance of the meniscus, on a scale at

TABLE V
LIQUID-VAPOR DENSITIES AT 9.50° C.

Average density	Liquid density	Vapor density	Weight liquid, gm.	Weight vapor, gm.	Total volume, cc.	Volume liquid, cc.	Volume vapor, cc.
0.1822*	0.188	0.1793	1.35	2.805	22.86	7.21	15.65
.1842*	.191	.1806	1.55	2.610	22.58	8.13	14.45
.2020	.2103	.192	3.654	2.77	31.78	17.38	14.40
.2032*	.2113	.191	2.498	1.66	20.52	11.82	8.70
.2070	.2154	.196	3.726	2.09	31.01	17.26	13.75
.2095	.2203	.194	3.965	2.46	30.64	17.99	12.65
.2153	.2255	.196	4.380	2.04	29.82	19.42	10.40
.2184	.2268	.201	4.490	1.93	29.40	19.80	9.60
.2210	.2283	.204	4.634	1.79	29.05	20.30	8.75
.2253	.2310	.210	4.670	1.73	28.50	20.25	8.25

* These values were obtained with an entirely new apparatus, and the ethylene was purified by means of a Podbielniak still.

the side of the bomb. The total volume at this mercury level could be calculated from the average density of the medium and the weight of ethylene. A plot of scale readings against volume gave the relative volumes of liquid and vapor from the position of disappearance of the meniscus. The amount and density of the phase not directly measured could then be calculated by difference. This procedure assumes the homogeneity of each phase, and is therefore not absolute, but such an assumption is the simplest and most obvious. The results are given in Table V, and shown graphically in Fig. 2. It will be noted, as indicated in the table, that the data are obtained from different samples of pure ethylene.

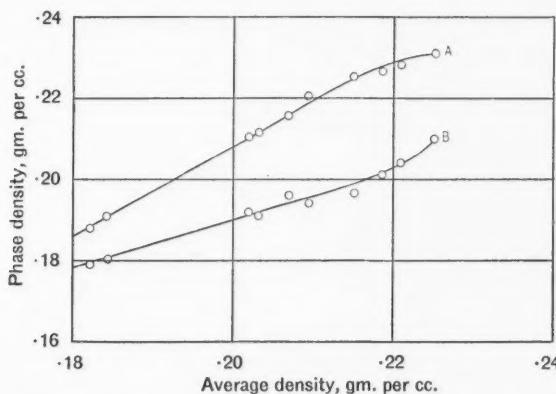


FIG. 2. Phase densities at 9.50° C. Upper curve, liquid. Lower curve, vapor

It is interesting to note that the vapor phase at one average density may have a greater density than the liquid at a lower average density. According to the classical theory there should exist no difference, and, from the definition of equilibrium, the nature of the two phases should be independent of the relative amounts of each phase. One is therefore led to the conclusion that either the densities determined are not equilibrium values, a point that cannot be directly settled since time is of infinite duration, or else some other factor besides the relative amounts of the phases is being altered as the mass per volume ratio is changed. This factor may well be the regional orientation, in the nomenclature of Maass and Geddes (7) or the cybotactic groups of Benz and Stewart (1).

For this reason the maximum divergence is to be expected at the critical density. At the critical density the movement of the meniscus should be a minimum, and therefore dilution of one phase by the other should also be a minimum. If the absolute values of Geddes and Maass were employed, the maximum would occur at a density of 0.2250 gm. per cc. and not at the critical. This simple explanation would therefore be invalidated; this is a good indication that the values now recorded are more nearly correct.

Constancy of Pressure with Changing Volume above the Critical Temperature

Recently Mayer and Harrison (6, 10) made some interesting calculations based on statistical mechanics as to what might be expected in the critical-temperature-critical-pressure region of a one component system. They have found experimental corroboration in the results obtained in this laboratory and went on to predict that the pressure of a system just above the critical temperature would remain constant with changing mass per volume. Specifically they predict a region above the critical temperature, as classically defined, in which the pressure-volume curves for various temperatures are characterized by $\left(\frac{\partial p}{\partial V}\right)_T = 0$. This region has an upper limit given by that temperature for which $\left(\frac{\partial p}{\partial V}\right)_T = 0$ for one point only. The isothermals of Geddes and Maass show no such region. However, the experimental points are not close enough together to settle this question definitely. The evidence given in Table VI shows the validity of Mayer and Harrison's prediction. Owing to the possible importance of this experiment the technique of manipulation may well be presented fully.

TABLE VI
DATA SHOWING CONSTANCY OF PRESSURE WITH CHANGING VOLUME AT 9.80° C.

Mercury level	Average density	Specific volume, cc.	Equilibrium density	Pressure
125	0.2178	4.591	0.2214	50.35
113	.2094	4.775	.2148	50.36
130	.2214	4.514	.2247	50.36
108	.2070	4.830	.2112	50.35

The mercury was adjusted so that the float would be completely immersed in liquid ethylene. The temperature of both the carbon dioxide and ethylene was then carefully raised, great care being taken to maintain the mercury at a constant level. The ethylene temperature was raised to 9.80° C., and the equilibrium density determined. This density measurement showed that the system had remained heterogeneous, for it was an equilibrium value, and differed from the average density at that volume. The carbon dioxide temperature was read, and the pressure corrected for the difference in the mercury levels in the two bombs.

Since the heterogeneity of the system has been shown to be destroyed by either isothermal expansion or compression, the following procedure was employed. After a pressure reading had been made, the mercury level was changed by heating or cooling the carbon dioxide slightly. The centre U-tube was then frozen by raising the dry-ice-acetone mixture about it, and the ethylene cooled to 7.51° C. As may be seen from Fig. 3, the ethylene has, below 8° C., regained its original characteristics. The temperature of the

ethylene was again raised to 9.80° C., and a density and pressure reading obtained with the new volume.

Complete Hysteresis Curve at Constant Volume

The complete hysteresis curve of ethylene, temperatures below the critical temperature being included, has been determined for the first time, and is shown in Fig. 3. The triangular points represent cooling from 10.5° C., a temperature at which the liquid phase has been nearly destroyed. No increase in density occurs on cooling until a visible meniscus forms. This has a bearing on the interpretation of the peculiar data obtained from air-ethylene mixtures, as will be shown later.

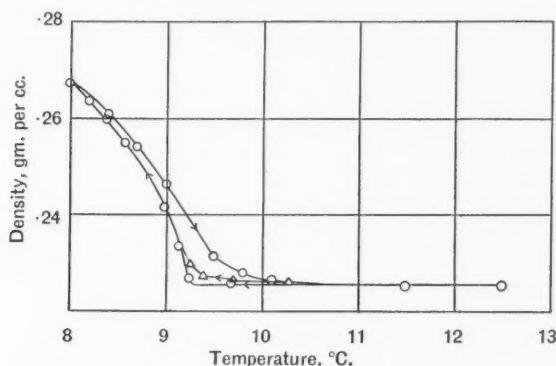


FIG. 3. Isochore of average density 0.2253. Triangular points denote cooling from 10.5° C.

AIR-ETHYLENE MIXTURES

A fortunate accident in the use of an ethylene sample contaminated with air had led to unexpected results with respect to the classical temperature-density curve. This sample did not yield the normal hysteresis curve of pure ethylene. The cooling curve followed the heating curve very closely. In order to determine a possible cause of such behavior, measured quantities of air and ethylene were introduced into the apparatus. Two samples, one 0.93% air by weight, the other 0.55% air, were studied.

Isobars of Air-ethylene Mixtures

Two isobars of each sample are given in Fig. 4. The time lags for both heating and cooling have already been recorded in Table III. The times to half-value agree, within the sensitivity of the method, with the values obtained for pure ethylene. Moreover, the shapes of the isobars are similar to those of the curves obtained with pure ethylene. These facts indicate that the inflections observed in isobar runs with pure ethylene are not noticeably affected by the presence of air in these concentrations. This is not so in isochore runs.

Another point of interest in these curves is the increase in density with decreasing air content. The reason for this is that the isobar systems, although at pressures well above the critical in both cases, are now not homogeneous systems (they would be if ethylene alone were present) but consist of two phases. The air is apparently largely insoluble in the liquid ethylene. This causes an increase in pressure on the system, and a corresponding increase in total volume, with a consequent decrease in the density.

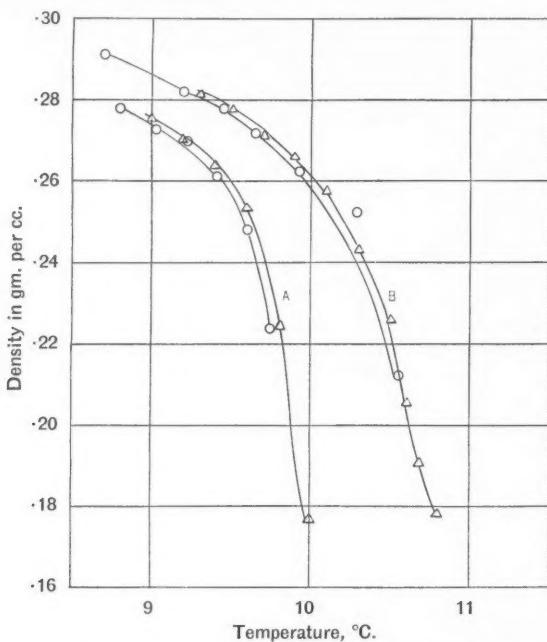


FIG. 4. Isobars of air-ethylene mixtures. Circles, 0.93% air. Triangles, 0.55% Air. A, 50.54; B, 51.44 atm.

Isochores of Air-ethylene Mixtures

These curves, of which typical examples are shown in Fig. 5, exhibit a behavior vastly different from that of the curves obtained with pure ethylene.

The greatest difference is the increase of density with decrease in temperature when the cooling is started above the critical, a phenomenon that has been noted for the first time.

In order to understand the complete significance of what is to follow, a brief review of previous work and theories is given.

The classical temperature-density curve has long been assumed to be parabolic in shape, with a smooth vertex. Experimental evidence had been obtained with increasing temperature nearly to the critical, but never quite

to it. The form of the curve was therefore extrapolated by means of the Cailletet-Mathias rule regarding the critical density. Traube (16), Galitzine (5), and Teichner (15) were the first to question this procedure, and recorded the observation of a density discontinuity above and below the position of disappearance of the meniscus, and that the meniscus reappeared at a temperature other than the critical. Young (20) and others failed to reproduce these results, and attempted to explain them by the theory that impurities hindered the establishment of equilibrium by slowing up of diffusion. Maass and his collaborators have traced the density-temperature curve through the entire critical region with very carefully purified materials, and confirmed the first results of Galitzine *et al.*

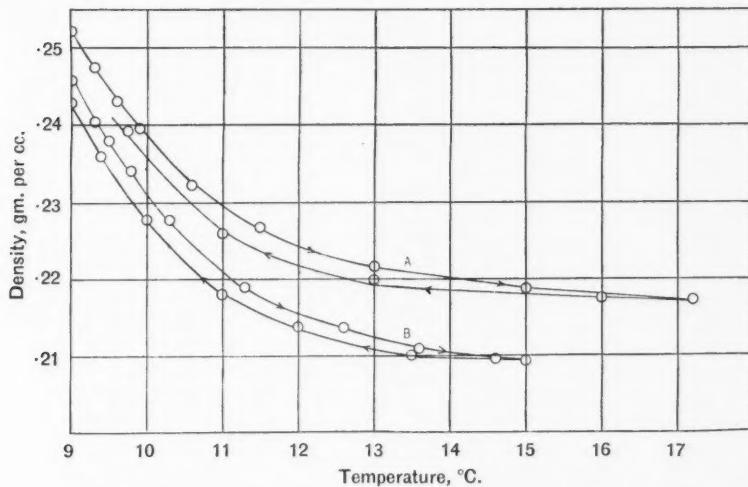


FIG. 5. Isochores of air-ethylene mixtures. A, 0.93% air; B, 0.55% air.

It is now believed by the present authors that if this behavior is caused by impurities, and this is regarded as improbable, a mechanism other than that proposed by Young must be assumed. Moreover, it seems doubtful that substances may be obtained pure enough for this phenomenon to disappear entirely, in the light of the work of Clark (2, 3) and that described in the present paper.

Turning again to the time lags of these runs, we see that the order of magnitude in the establishment of equilibrium density is now quite different and much smaller. This in itself indicates an entirely different type of phenomenon to be occurring. There appear two alternatives in explaining what is happening. First, either the liquid phase is destroyed and reformed, and that much more quickly in the presence of air; or second, the air causes the liquid state to persist, since it apparently is not dissolved to any great extent, by

increasing the pressure on that phase. In this case the changes of density may easily be explained by an expansion or contraction of the liquid.

A rough calculation for the 0.93% mixture gives, on the assumption that the meniscus is in the middle of the tube, and that the air is immiscible with liquid ethylene, an excess pressure of approximately three atmospheres. Certain "molecular stirring" experiments performed in the following manner support this theory.

TABLE VII
MOLECULAR STIRRING

Intermittent stirring nearly completely destroys liquid

Density	Time of stirring, min.	Temp., °C.	No. of stirrings
0.2379	0	10.00	0
.2215	25	10.00	1
.2193	21	10.00	2
.2172	15	10.00	3
.2172	12	10.00	4

System was cooled to 9.60° C. The density increased slightly to 0.2177 gm. per cc. If heated to 13.5° C., after such stirring the density falls to 0.2160 gm. per cc. On cooling from 13.5° C., the density changes as follows:—

Density	Temp., °C.	Density	Temp., °C.
0.2160	12.50	0.2211	9.40
.2166	11.00	.2227	9.10
.2182	10.00	.2355	8.90
.2197	9.60		

Condensation occurs at approximately 9.0° C.

now lowered. As shown in Fig. 3, when the liquid phase is partly destroyed, no increase in density occurs on cooling. From this and the above experiments we are led to the conclusion that the liquid phase had persisted many degrees above the critical, owing to the pressure caused by the presence of the inert gas. This allows of the possibility that the phenomenon of hysteresis might entirely disappear if the purity of the substance were great enough. The care taken in purification and filling the apparatus with the pure ethylene samples makes this seem, however, a very remote one.

These investigations are being continued. Particularly the influence of added impurities, both inert and soluble ones, may help to elucidate the nature of the phenomenon. At present the most general explanation that seems plausible is that the liquid state of aggregation differs from the gaseous state

A cooling coil was wound around the upper portion of the bomb. The coil could be maintained at 5° C. by the passage of tap water through it. The temperature of the bomb was raised to 10° C., the sliding thermostat partly lowered, and the upper portion of the bomb cooled. Violent distillation occurred, and the liquid phase was destroyed, since all parts of the sample were subjected to alternate heating and cooling. After several stirrings of this kind, and subsequent heating to 13.5°, the sample had a density of 0.2160 gm. per cc., as Table VII shows. The system is now probably homogeneous, and on cooling acts much like pure ethylene, as Fig. 6 shows, except that the temperature of condensation is

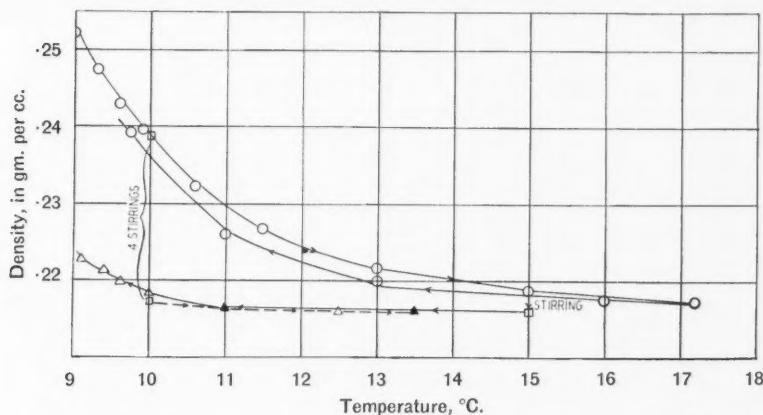


FIG. 6. Molecular stirring. Circles denote reference isochore; triangles denote behavior on heating to 13.5° C. after stirring, then cooling; squares denote behavior on stirring; block triangles denote behavior subsequent to stirring.

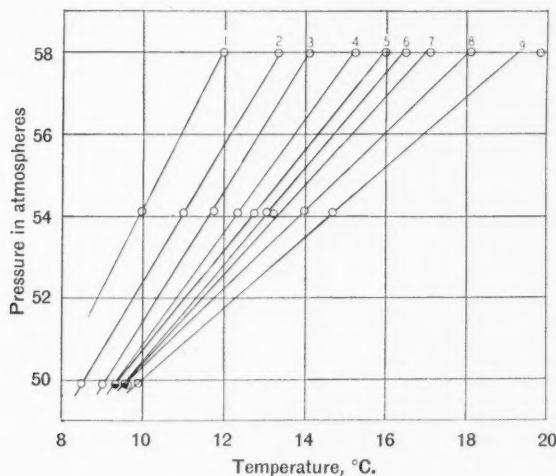


FIG. 7. Pressure-temperature relations for various isochores evaluated from Geddes and Maass's isobars. Numbers denote following isochores—1, 0.290; 2, 0.275; 3, 0.262; 4, 0.240; 5, 0.220; 6, 0.205; 7, 0.190; 8, 0.170; 9, 0.148 gm. per cc. Shaded circles denote double points.

owing to a structure in the former. At the critical temperature and pressure the density of the liquid has been reduced to a point at which structure tends to disappear. Increase in pressure above the critical temperature tends to re-establish structure.

References

1. BENZ, C. A. and STEWART, G. W. Phys. Rev. 46 : 703-706. 1934.
2. CLARK, A. L. Trans. Roy. Soc. Can. III, 9 : 43-67. 1915.
3. CLARK, A. L. Trans. Roy. Soc. Can. III, 18 : 329-338. 1924.
4. EDWARDS, J. and MAASS, O. Can. J. Research, 12 : 357-371. 1935.
5. GALITZINE, B. Wied. Ann. 50 : 521-545. 1893.
6. HARRISON, S. F. and MAYER, J. E. J. Chem. Phys. 6 : 101-104. 1938.
7. MAASS, O. and GEDDES, A. L. Phil. Trans. Roy. Soc. A, 236 : 303-332. 1937.
8. MARSDEN, J. and MAASS, O. Can. J. Research, B, 13 : 296-307. 1935.
9. MARSDEN, J. and MAASS, O. Can. J. Research, B, 14 : 90-95. 1936.
10. MAYER, J. E. and HARRISON, S. F. J. Chem. Phys. 6 : 87-100. 1938.
11. MILLS, J. E. J. Phys. Chem. 9 : 402-417. 1905.
12. MORRIS, H. E. and MAASS, O. Can. J. Research, 9 : 240-251. 1933.
13. SUTHERLAND, H. S. and MAASS, O. Can. J. Research, 5 : 48-63. 1931.
14. TAPP, J. S., STEACIE, E. W. R. and MAASS, O. Can. J. Research, 9 : 217-239. 1933.
15. TEICHNER, G. Ann. Physik, 13 : 595-610. 1904.
16. TRAUBE, J. Z. anorg. allgem. Chem. 38 : 399-409. 1904.
17. WINKLER, C. A. and MAASS, O. Can. J. Research, 6 : 458-470. 1932.
18. WINKLER, C. A. and MAASS, O. Can. J. Research, 9 : 65-79. 1933.
19. WINKLER, C. A. and MAASS, O. Can. J. Research, 9 : 613-629. 1933.
20. YOUNG, F. B. Phil. Mag. 20 : 793-828. 1910.

THE MERCURY PHOTOSENSITIZED DECOMPOSITION OF ETHANE

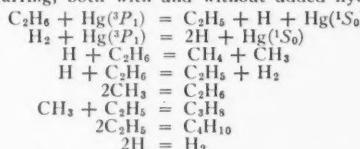
II. THE PRODUCTION OF HYDROGEN AND THE MECHANISM OF THE REACTION¹

BY E. W. R. STEACIE² AND N. W. F. PHILLIPS³

Abstract

An investigation of the mercury photosensitized decomposition of ethane has been made, a continuous flow system being used. Under these circumstances, in the absence of secondary reactions, it is found that there is considerable production of hydrogen. It is therefore concluded that the primary step in the reaction is a C—H bond split.

The mechanism of the reaction is discussed in detail, and it is concluded that the processes occurring, both with and without added hydrogen, are:



It is also concluded from a discussion of the various steps that the reaction



is somewhat faster than



This necessitates a revision upwards of Steacie and Phillips' estimate of the activation energy of the latter reaction to about 9 Kcal.

Introduction

The mercury photosensitized decomposition of ethane has been examined in a qualitative manner by Tolloczko (17), Taylor and Hill (15), and Kemula (2). A more detailed investigation of the reaction was made by Kemula, Mrazek, and Tolloczko (3). In their experiments the reaction mixture was circulated through a trap at -80°C . in an attempt to remove the products of the reaction as fast as formed, and thus prevent secondary processes. This attempt was not very successful, since more than half of their products were of a molecular weight higher than that of butane, and hence could have resulted from secondary changes only. The analysis of their products was only roughly performed, and consequently the results of their experiments were not very significant.

A more thorough investigation in which the secondary decomposition of higher products was entirely eliminated has recently been made by Steacie and Phillips (13). The essential features of their technique were the employ-

¹ Manuscript received July 5, 1938.

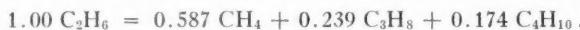
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada, with financial assistance from the National Research Council of Canada.

² Associate Professor of Chemistry, McGill University.

³ At the time, Demonstrator in Chemistry, McGill University. Present address: National Research Laboratories, Ottawa, Canada.

ment of powerful light sources, low temperature distillation methods of analysis, and more efficient trapping methods for the removal of higher products.

By operating with a trap cooled to -130° C., they found that the products of the reaction consisted entirely, within the experimental accuracy of 0.3%, of methane, propane, and butane, as expressed by the stoichiometric equation



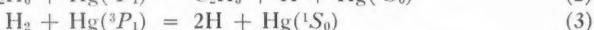
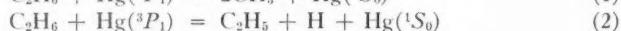
The quantum yield in terms of ethane disappearing was found to be about 0.2.

If the decomposition were carried out in the presence of added hydrogen, the yield of methane was increased and hydrogen was consumed, as indicated by the average stoichiometric equation

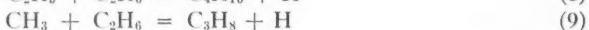
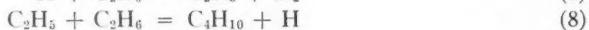
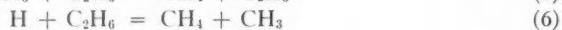


In discussing the mechanism of the reaction, they considered the following steps:

Primary Reactions



Secondary Reactions of Radicals or Atoms with Ethane



Radical and Atom Recombination Reactions



Other Secondary Reactions of Radicals



Reactions Involving the Methylidene Radical



They thus considered three possible primary processes for the decomposition of the ethane molecule, *viz.*,

- (a) the elimination of a methylidene radical;
- (b) a C—H bond split to give an ethyl radical and a hydrogen atom;
- (c) a C—C bond split to give two methyl radicals.

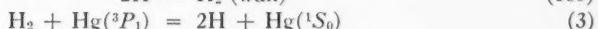
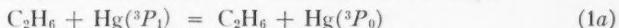
If Reaction (4) were the primary step, propane and butane formation would have occurred by Reactions (20) and (21), and thus at the lowest trapping temperatures the formation of butane should have ceased. As this was not the case, and for other reasons discussed at length in their paper, Steacie and Phillips considered Reaction (4) to be very unlikely as the primary step.

In considering Reaction (2) as the initial process, they assumed the subsequent steps to be Reactions (6), (5), (10), (11), (12), (14), and (15). They pointed out that the main difficulty to be overcome by any mechanism which assumes a primary C—H split would be to account for the absence of hydrogen in the products of the reaction. By assuming that hydrogen atoms, if formed, were consumed chiefly by Reaction (6), and that molecular hydrogen was formed by Reaction (13), *i.e.*, by diffusion to the wall, they calculated that the quantity of hydrogen formed on this basis during an experiment would be from 30 to 200 times the minimum detectable amount. They therefore concluded that a mechanism involving a C—H bond split was inconsistent with experiment, and that the initial step was a C—C bond split (Reaction (1)), followed by Reactions (5), (10), (11), and (15).

The Tenability of a Mechanism Involving a C—H Split

An examination of the reasoning which led to the discarding of the possibility of a C—H split for the primary process shows that re-dissociation of molecular hydrogen by Reaction (3) has been assumed to be negligible. In view of the large cross section of hydrogen relative to ethane for the quenching of 3P_1 mercury atoms, it was decided that it was possible that Reaction (3) might be of importance in reducing the concentration of molecular hydrogen in the system.

In order to evaluate the upper limit of the hydrogen concentration under these circumstances, let us consider the following reaction steps:



From this scheme a steady state concentration of hydrogen can be deduced. Hydrogen formation will occur by Reactions (7), (13a), and (13b), and its destruction by (3). Hence we have

$$\begin{aligned} \frac{d[H_2]}{dt} &= 0 \\ &= \frac{[H_2]\sigma_1^2\mu_1^{1/2}I_{abs}}{[C_2H_6]\sigma_2^2\mu_2^{1/2} + [H_2]\sigma_1^2\mu_1^{1/2}} \\ &\quad - f \left(\frac{[C_2H_6]\sigma_2^2\mu_2^{1/2}eI_{abs}}{2([C_2H_6]\sigma_2^2\mu_2^{1/2} + [H_2]\sigma_1^2\mu_1^{1/2})} + \frac{[H_2]\sigma_1^2\mu_1^{1/2}I_{abs}}{[C_2H_6]\sigma_2^2\mu_2^{1/2} + [H_2]\sigma_1^2\mu_1^{1/2}} \right), \end{aligned}$$

where σ_1 and σ_2 are the mean quenching diameters of excited mercury and hydrogen and excited mercury and ethane respectively; μ_1 and μ_2 , their respective reduced masses; I_{abs} is the resonance radiation absorbed in einsteins per sec.; e is the efficiency of Reaction (2) relative to (1a) plus (2), i.e.,

$$e = \frac{k_2}{k_{1a} + k_2},$$

and f is the fraction of hydrogen atoms which react to form H_2 . This last quantity is given by

$$f = \frac{k_7[H][C_2H_6] + k_{13a}[H]^2[C_2H_6] + \frac{k_{13b}[H]}{[C_2H_6]}}{k_7[H][C_2H_6] + k_{13a}[H]^2[C_2H_6] + \frac{k_{13b}[H]}{[C_2H_6]} + k_6[H][C_2H_6]}.$$

Whence we get

$$\frac{[H_2]}{[C_2H_6]} = \frac{ef}{2r(1-f)},$$

where

$$r = \frac{\sigma_1^2\mu_1^{1/2}}{\sigma_2^2\mu_2^{1/2}} = 60.$$

Now in the experiments performed at the lower trapping temperatures, as in Runs 7 and 8 of Table II of the previous paper, the amount of ethane in the gas phase was only about one-tenth of the total amount present owing to condensation in the traps. Hence if we assume as an extreme case $e = 1$, $= 0.9$, then the percentage of hydrogen which should be found in the products of the reaction is 0.75, which is only two or three times the sensitivity of the analytical method used. If we make the more reasonable assumption that $e = 0.5$ and $f = 0.5$, then the amount of hydrogen which should be found in the products is 0.04%, which would have been quite undetectable by the analytical methods employed.

It is therefore possible that the decomposition occurs by an initial C—H bond split. Of course, although this analysis indicates that a C—H split is possible, it offers no proof that it actually occurs as the primary step in the reaction. It was to establish this point with certainty that the present experi-

ments were performed. A continuous (*i.e.*, single pass) flow system was employed. By this method the concentration of hydrogen, if formed, would be kept low, and hence the back reaction, (3), would be diminished; this would permit the hydrogen to accumulate in the products.

The Reaction System

Experimental

The main portion of the apparatus is shown in Fig. 1. The gas at constant pressure entered the system through a calibrated capillary flowmeter. It then flowed through the mercury saturator, *S*, a desaturating trap, *D*, and the light-source-reaction vessel. The saturator, *S*, provided a mercury surface of about 30 cm². and was electrically heated to 60 to 80° C. The trap, *D*, of about 100 cc. capacity, was packed with small iron pellets. Suitable tests showed that this completely removed the excess mercury picked up by the gas in *S*, and thus the mercury vapor pressure could be regulated by adjusting the temperature of the thermostat surrounding *D*.

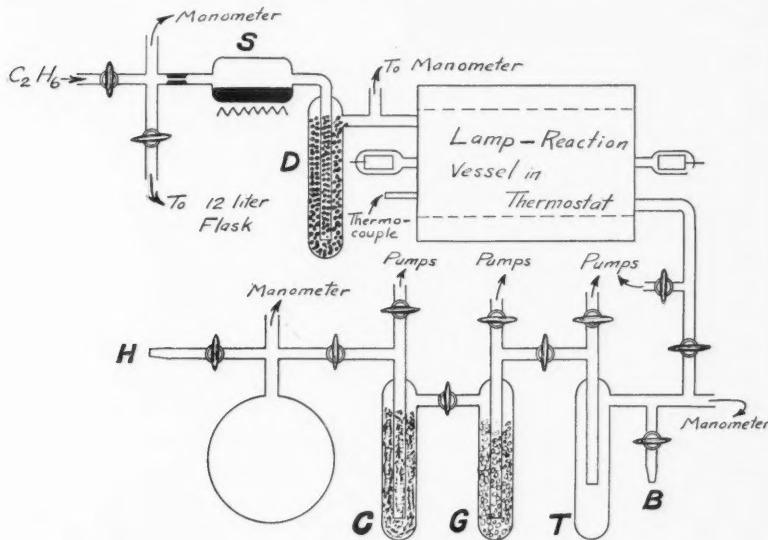


FIG. 1. Apparatus.

The light-source-reaction vessel arrangement has already been described (14). It made possible the utilization of the very high output of mercury resonance radiation of 1.5×10^{-5} einsteins per sec.

The pressure in the reaction vessel was regulated by controlling the outflow of the gases, a file-scratched stopcock being used as an adjustable leak. The gas flowed through this stopcock into three traps, *T*, *G*, and *C*, cooled to -183° C. The first trap was initially empty, the second packed with

silica gel, and the third with activated charcoal. A 500 cc. expansion bulb and a manometer were connected to the charcoal trap. The first trap served to collect any higher products and all the ethane. The second and third took out methane and hydrogen. The total amount of these gases could be inferred by isolating the traps and the expansion bulb and warming the traps to room temperature.

The different parts of the apparatus could be separately evacuated as indicated, and ground joints *B* and *H* attached to the collecting traps made provision for the transfer of gases to the analytical system.

The Analytical System

The analytical system consisted of a low temperature fractional distillation apparatus of the Podbielniak type. The column was of small dimensions, and the apparatus could thus be used for the analysis of relatively small samples. With 500 to 600 cc. of gas an accuracy of about 0.3% could be attained. In the analysis the methane and hydrogen were taken off together, and their separate amounts determined by combustion. The method of carrying out the combustion analysis was somewhat novel, and is very convenient for use with a vacuum system. A diagram of the combustion apparatus is given in Fig. 2.

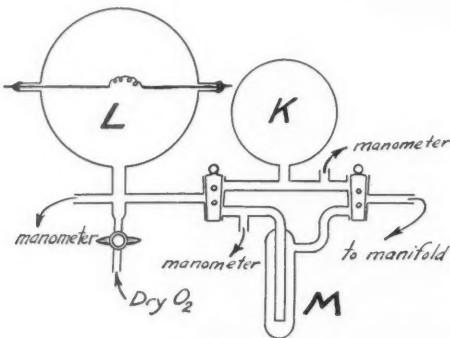


FIG. 2. Combustion apparatus.

The combustion pipette, *L*, has a volume of about two litres, and contains an electrically heated platinum spiral of the usual type. Oxygen, which has been dried by passage through a liquid air trap, can be led in as indicated. The gas sample is expanded from the manifold of the distillation apparatus into the bulb *K* of known volume, and its pressure is read on the manometer. The gas from *K* is then expanded into *L*, which has been previously evacuated. It is not necessary to read the pressure in *L*. Oxygen is then run in and the combustion carried out as usual. The gases from *L* are then pumped out through the trap *M*, which is immersed in liquid air. Carbon dioxide and water from the combustion are thus retained, and oxygen is pumped away. *M* is then allowed to warm up to room temperature. The pressure in *M*

minus the vapor pressure of water thus gives the amount of carbon dioxide formed. Whence, knowing the relative volumes of K , L , and M , we can calculate the percentage of methane in the sample.

Materials

Ethane was obtained in cylinders from the Ohio Chemical and Mfg. Co. It was stated to be 97% pure. Analysis showed it to contain 1.3% of ethylene, less than 0.3% of hydrogen plus methane, and less than 0.3% of higher hydrocarbons.

The cylinder gas was purified by passage through a 60 cm. tube containing copper oxide at 300° C., through saturated bromine water into a two-litre bottle illuminated by a Point-o-lite lamp, through a 40% solution of potassium hydroxide, and finally through a trap at -80° C. to remove water. The resultant ethane contained no impurities which could be detected with the analytical method used.

Light Intensity

The measurement of the light intensity, and the determination of the amount of resonance radiation absorbed have been previously described (14).

Experimental Procedure

In making an experiment, the lamp was first run for 30 min. to ensure that it had reached a steady state. The saturator was heated, the traps were cooled, and the ethane flow was then started and continued for a definite period of time. Blank experiments showed that only hydrogen and methane collected in the packed traps, and that no appreciable amount of hydrogen was dissolved in the ethane in the unpacked trap. After the experiment the hydrogen-methane fraction was transferred to the analytical system, and the hydrogen was determined by combustion.

Results

The results of a number of experiments are given in Table I.

TABLE I

THE PRODUCTION OF HYDROGEN IN THE MERCURY PHOTOSENSITIZED DECOMPOSITION OF ETHANE
Ethane flow, 3.0 cc. per sec. at N.T.P. Mercury vapor pressure, 1.3×10^{-3} mm.
Resonance radiation absorbed, 1.2×10^{-5} einsteins per sec.

Run No.	Time, min.	Pressure, cm.	Temperature, °C.	Hydrogen formation, moles per sec. $\times 10^6$	Moles of hydrogen formed per quantum absorbed
1	30	4.3	90	0.96	0.080
2	30	4.3	67	1.03	0.086
3	30	4.3	67	0.94	0.078
4	61	4.8	65	0.95	0.079
5	30	4.3	-	0.00 }	
6	60	4.3	-	0.00 }	Blank runs, are not on.
7	30	4.3	450	5.5	0.48

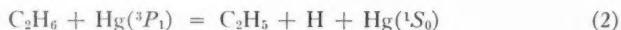
It may therefore be concluded that, in contrast to the results of the experiments in a circulatory system, hydrogen appears in large quantities when its partial pressure is kept down by the rapid removal of the products of the reaction. The quantum yield for its formation under these circumstances is about half as great as that based on the disappearance of ethane in the circulatory system. It will also be observed from Table I that the production of hydrogen rises rapidly with increasing temperature.

Discussion

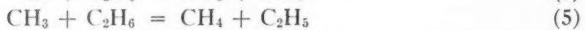
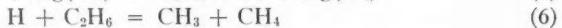
It follows from the above results that it is no longer necessary to rule out a C—H bond split mechanism. In fact, it now appears certain that the primary step must involve such a split, *i.e.*, that it must be Reaction (2). The only other alternative would be a C—C split followed by some reactions of methyl or ethyl radicals which produce hydrogen. The only possible reactions of this type would appear to be (8), (9), or (18), and there is no doubt that these are too slow to account for the observed hydrogen production.

Accepting a C—H bond split as the primary step, we then have as alternatives the following schemes:

Scheme I



Scheme II



These schemes assume the same primary step, and the same radical recombination reactions to produce the final products. They differ fundamentally, however, in the presence or absence of Reaction (5) as a means of production of ethyl radicals and of loss of methyl radicals.

With appropriate assumptions as to the relative rates of the various steps we can account stoichiometrically for the products of the reaction on either basis. However, general evidence from other investigations seems to indicate that Reaction (5) is slow compared to (6) and (7). Rice (9) assigned a value of 17 Kcal. to the activation energy of Reaction (5), and while this estimate is

perhaps high it is probably of the right order of magnitude. It may therefore be assumed with considerable plausibility that Reaction (5) is slow, and Scheme II is ruled out. This view is confirmed emphatically by recent work done at Princeton. Concerning this Prof. H. S. Taylor writes (16) ". . . all the evidence we have had for methane producing processes, starting from methyl, seems to lead to the conclusion that such processes were slow. With methyl iodide and with metal alkyls it was necessary to assume activation energies of 10 Kcal. or more. Morikawa found 11 to 15 Kcal. for the interaction of methyl and deuteromethane. I have had some experiments made . . . on the photodecomposition of mercury dimethyl, causing this to take place in the presence of ethane and determining at 35, 90, and 160° whether any methane was formed. There are negligible amounts at the two lower temperatures and very much less at 160° than we would have got with the hydrogen in place of ethane. This indicates that the activation energy must be more than 10 Kcal."

We may therefore consider Scheme I to be established. The low quantum yield may be ascribed partly to inefficiency in the primary process, perhaps by the occurrence of



and also partially by the occurrence of Reaction (10), leading to the reformation of ethane. This question will be discussed further in a communication dealing with the reaction in the presence of deuterium.

In discussing the results obtained at higher temperatures, it seems that the obvious explanation lies in an increase in the rate of Reaction (7) as compared with (6), as would be expected from its higher activation energy (see later). This is in accord with the results of Trenner, Morikawa, and Taylor (18), who found that at higher temperatures Reaction (7) became predominant. This process would also lead to an increased production of ethyl radicals, and the higher yields of butane relative to propane confirm this idea.

The Reaction in the Presence of Hydrogen

On account of the very high quenching efficiency of hydrogen, a simple calculation shows that in all the hydrogen-ethane mixtures used in the previous investigation the hydrogen was responsible for at least 99% of the quenching. Hence Reaction (3) is established with certainty as the primary step. In the circulatory system, as the reaction proceeds, a considerable quantity of methane is produced which remains in the gas phase. However, this methane, owing to its very small quenching cross section, will absorb only a negligible amount of the incident energy.

Since methane is formed and hydrogen consumed in the reaction, there seems to be no doubt that Reaction (6) is the predominating methane producing step. The only other ways of producing methane involve methyl radicals, and since Reaction (6) is the only reaction producing these in relatively large amount, it would seem to be established with certainty.

To explain the formation of butane it is necessary to have a step which produces ethyl radicals. The only possible reactions of this type appear to be (5) or (7), and as we have seen from the previous section Reaction (5) may be ruled out. The evidence available for Reaction (7) indicates an activation energy in the neighborhood of 9 Kcal. (12, 18), which would be sufficiently fast.

The next question to be answered is how satisfactorily will these reactions account for the results on a stoichiometric basis. First, we may consider the mode of disappearance of the atoms and radicals. Present evidence seems to be in favor of assigning rapid rates to recombination reactions such as (10), (11), and (15) (see, for example, (8)). Reactions producing hydrogen atoms such as (9), or



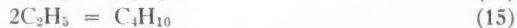
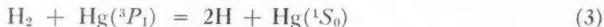
are generally considered to have high activation energies, possibly of the order of 15 to 20 Kcal. (9). The occurrence of Reactions (16) and (17) presents some possibility because of the concentration factors in their favor. Leermakers (4) puts $E_{16} = 15$ Kcal. For E_{17} we have estimates (1, 6, 7, 10) from 8 to 23 Kcal., though the best evidence seems to be in favor of a value lower than 15 Kcal. The occurrence of Reactions (16) and (17) to any great extent, however, would lead to too high a value for the ratio

$$\frac{\text{hydrogen consumed}}{\text{methane produced}},$$

as well as suggesting chain characteristics which would not be in accord with the low quantum yield.

Recombination of hydrogen atoms, it would seem, could hardly compete with radical recombination reactions, since there are no reasons for assuming very different orders of concentration for the atoms and radicals, and as the reactions involving atoms are more inefficient owing to third body restrictions (see, for example (5)).

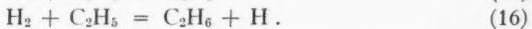
We therefore have as the mechanism of the reaction:



This mechanism accounts completely for the products of the reaction, provided that we assume that Reaction (6) is about four times as fast as (7).

The only way to avoid such an assumption would be to postulate some reaction of velocity comparable to that of (7) which consumes hydrogen and destroys ethyl radicals. The former requisite is necessary to account for the over-all hydrogen consumption, and the latter to account for the low yield

of propane and butane relative to methane. The only possible reactions seem to be



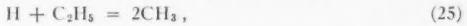
In view of the low concentrations of both colliding partners and the dreierstoss restrictions on (14), its occurrence with sufficient rapidity is impossible. The unlikelihood of the occurrence of Reaction (16) has already been mentioned, and results obtained on the reaction with deuterium, to be reported later, also rule it out*.

Apparently, then, it must be assumed that Reaction (6) is about four times as fast as (7). Steacie and Phillips (12) originally found an activation energy of 6.3 Kcal. for (7). This value, however, is now open to some question, since they did not take into account the possibility of the formation of methane in the reaction of hydrogen atoms with ethane. Trenner, Morikawa, and Taylor (18) estimated $E_6 = 7.2$ Kcal., $E_7 = 11.4$ Kcal. Steacie (11) in a further investigation reported $E_6 = 8.6$ Kcal. The present results, by requiring Reaction (6) to be four times as fast as (7) necessitate a revision upward of our previous estimate of E_7 to about 9 Kcal., which is approaching the value reported by Trenner, Morikawa, and Taylor.

References

1. v. HARTEL, H. and POLANYI, M. Z. physik. Chem. B, 11 : 97-138. 1930.
2. KEMULA, W. Roczniki Chem. 10 : 273-286. 1930.
3. KEMULA, W., MRAZEK, S., and TOLLOCZKO, S. Collection Czechoslov. Chem. Commun. 5 : 263-278. 1933.
4. LEERMAKERS, J. A. J. Am. Chem. Soc. 56 : 1899-1904. 1934.
5. MORIKAWA, K., BENEDICT, W. S., and TAYLOR, H. S. J. Chem. Phys. 5 : 212-225. 1937.
6. PANETH, F. A., HOFEDITZ, W., and WUNSCH, A. J. Chem. Soc. (London), 372-379. 1935.
7. PATAT, F. Z. Physik. Chem. B, 32 : 274-293. 1936.
8. RICE, F. O. and HERZFIELD, K. F. J. Am. Chem. Soc. 56 : 284-289. 1934.
9. RICE, F. O. and RICE, K. K. The aliphatic free radicals. Johns Hopkins Press, Baltimore. 1935.
10. SICKMAN, D. V. and RICE, O. K. J. Chem. Phys. 4 : 608-613. 1936.
11. STEACIE, E. W. R. J. Chem. Phys. 6 : 37-40. 1938.
12. STEACIE, E. W. R. and PHILLIPS, N. W. F. J. Chem. Phys. 4 : 461-468. 1936.
13. STEACIE, E. W. R. and PHILLIPS, N. W. F. J. Chem. Phys. 6 : 179-187. 1938.
14. STEACIE, E. W. R. and PHILLIPS, N. W. F. Can. J. Research. B, 16 : 219-221. 1938.
15. TAYLOR, H. S. and HILL, D. G. J. Am. Chem. Soc. 51 : 2922-2936. 1929.
16. TAYLOR, H. S. Private communication.
17. TOLLOCZKO, S. Przemysl Chem. 11 : 245-253. 1927.
18. TRENNER, N. R., MORIKAWA, K., and TAYLOR, H. S. J. Chem. Phys. 5 : 203-211. 1937.

*In a recent private communication, Professor Taylor suggests that it is possible that Reaction (7) is nevertheless faster than (6), if we assume that we have as an important reaction



followed by



The main trouble with such a mechanism from our point of view is that by requiring all the methyl radicals to be formed via ethyl, it is difficult to see how the butane formation can be suppressed sufficiently so that large amounts of methane are produced.

This suggestion would, however, give a very simple explanation of Trenner, Morikawa and Taylor's results, since assuming a low activation energy for Reaction (25), its rate would not increase as much as that of (7) as the temperature was raised. As a result the concentration of atomic hydrogen would decrease, that of ethyl would increase, and there would be less methane production at higher temperatures.

THE MERCURY PHOTOSENSITIZED DECOMPOSITION OF ETHANE

III. THE REACTION IN THE PRESENCE OF ADDED DEUTERIUM¹

BY E. W. R. STEACIE², W. A. ALEXANDER³, AND N. W. F. PHILLIPS⁴

Abstract

The mercury photosensitized reactions of ethane-deuterium mixtures have been investigated. The products of the reaction were separated by low-temperature fractional distillation, and the deuterium content of each was determined. It was found that the methane produced was highly deuterized, while the residual ethane was only slightly deuterized. Propane and butane were also considerably deuterized. It is concluded:

- (a) That rapid exchange of methyl radicals and deuterium atoms occurs, as previously suggested by Morikawa, Benedict, and Taylor;
- (b) That ethyl radicals are rapidly exchanged in a similar way;
- (c) That the reactions



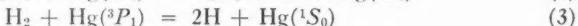
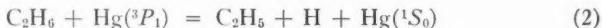
and



do not occur to any great extent, and hence the low quantum yield of the reaction cannot be ascribed to re-formation of ethane.

Introduction

The results of an investigation of the mercury photosensitized decomposition of ethane and a discussion of the mechanism of the reaction have been given in previous papers (5, 6, 7). Experiments have also been reported on the reaction in the presence of hydrogen. It was concluded that the processes occurring both in the presence and in the absence of added hydrogen can be adequately accounted for by the following reactions. (The numbering of these reactions is the same as that used in (7).)



It is possible to obtain considerable information on certain points by the substitution of deuterium for hydrogen, and an examination of the distribution of deuterium among the products of the reaction. The present paper deals with experiments of this kind.

¹ Manuscript received July 5, 1938.

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada, with financial assistance from the National Research Council of Canada.

² Associate Professor of Chemistry, McGill University.

³ Holder of a Studentship under the National Research Council of Canada.

⁴ At the time, Demonstrator in Chemistry, McGill University. Present address: National Research Laboratories, Ottawa, Canada.

*Apparatus and Procedure***Experimental**

The apparatus has already been described (7). It consisted essentially of storage bulbs for the reactants, a circulation system, and a pumping system. Circulation was accomplished by means of a reciprocating pump and a series of mercury valves so arranged that the gases always flowed in one direction. The gases were saturated with mercury vapor by passing them over a heated mercury surface at 60 to 80° C., and then through a trap at 20° C. to remove the excess vapor. The gases then passed through the illuminated reaction vessel, through a trap at -130° C. to remove the reaction products of higher molecular weight, and thence back to the circulating pump. At the end of a definite time of reaction, the lamp was shut off, the pump stopped, and the cold trap allowed to warm up to room temperature.

The gases were then pumped by means of a Toepler pump into a portable mercury gas holder, and transferred to a low-temperature fractional distillation apparatus of the Podbielniak type. The separated fractions from the still were burned, the resulting water was decomposed on a heated tungsten filament, and the resulting hydrogen was analyzed for its deuterium content. The deuterium analysis apparatus was a modified high pressure, high temperature thermal conductivity apparatus similar to that used by Melville and Bolland (1, 3).

Materials

The ethane used was obtained from the Ohio Chemical and Mfg. Co., and was purified by distillation in a still of the Podbielniak type.

The deuterium used in the first run was obtained by the decomposition of 99.6% deuterium oxide by metallic magnesium at 480° C. (2). The deuterium used in Experiments 2 and 3 was obtained by the decomposition of deuterium oxide with metallic calcium. In both cases the gas was dried by passage through a liquid air trap before use.

Results

Three runs were made, different proportions of ethane and deuterium being used. The operating conditions, etc., are given in Table I. The total initial pressure given in the table was observed with the whole system at room temperature.

The analyses of the products are given in Table II. In the analysis the products were separated into five fractions, hydrogen + methane, methane, ethane, propane, and butane. No other products were detected. The percentages of methane and hydrogen in the first fraction were determined by combustion in the ordinary way.

The deuterium contents of the reactants and products, and the input and yield of the process with respect to hydrogen and deuterium are given in Table III. The total hydrogen value given in Column 4 in terms of mole-atoms includes the quantities of hydrogen and deuterium in the various substances, and is obtained by multiplying the mole percentage of each substance in the products, as given in Table II, by the number of hydrogen

atoms in the molecule. The total deuterium content of each substance given in Column 5 is obtained by multiplying the figures in Columns 3 and 4. It is evident from the deuterium balance shown in the final column that the losses of deuterium are very small, when the large number of operations through which the gases have gone are considered.

TABLE I
THE MERCURY PHOTOSENSITIZED DECOMPOSITION OF ETHANE IN THE PRESENCE OF DEUTERIUM

Volume of system, 2180 cc.	Arc current, 0.100 amp.
Mercury vapor pressure, 1.3×10^{-3} mm.	Arc potential, 495 volts.
Circulation rate—	Resonance radiation absorbed, 1.5×10^{-5} einsteins per sec.
3 litres per min. in Run 1	Trap temperature, -130° C.
6 litres per min. in Runs 2 and 3	Ethane vapor pressure, about 4 cm.
Temperature of reaction vessel, 75° C.	

Run No.	Time, min.	Initial ratio D_2 / C_2H_6	Total initial pressure, cm.	Fraction of C_2H_6 decomposed	Rate of C_2H_6 decomposition, moles per sec. $\times 10^6$	Quantum yield	Products, moles per mole of ethane decomposed			
							D_2 (consumed)	CH_4 (formed)	C_3H_8 (formed)	C_4H_{10} (formed)
1	75	0.52	31.6	0.51	2.74	0.182	0.23	1.01	0.10	0.12
2	90	1.00	34.2	0.66	2.48	0.165	0.43	1.21	0.10	0.12
3	83	1.83	63.5	0.39	1.95	0.130	0.38	1.13	0.12	0.13

TABLE II
DETAILS OF THE ANALYSES

Run No.	Hydrogen-methane fraction		Final percentages of the products of reaction				
	CH_4	H_2	H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}
1	18.8	81.2	26.4	33.7	32.5	3.4	4.0
2	12.1	87.9	35.8	39.9	17.0	3.3	4.0
3	9.1	90.9	59.4	15.6	21.5	1.7	1.8

Discussion

The most noteworthy points in the above results are:

- (a) The very high deuteration of methane;
- (b) The low deuteration of ethane;
- (c) The quite high deuteration of propane and butane.

On the basis of Steacie and Phillips' mechanism for the reaction, the main method of methane formation is



together with a certain amount by



Obviously if all the deuteration of methane occurred in this manner, the maximum possible deuterium content of the methane would be one-quarter

that of the hydrogen present. Actually, as shown in Table III, the D-content of the methane is from 50 to 85% that of the hydrogen at the end of the experiment, *i.e.*, it is approaching complete distribution of deuterium between methane and hydrogen, rather than one-quarter of such a distribution.

Similar behavior was found in the reaction between deuterium atoms and methane by Morikawa, Benedict, and Taylor (4). They suggested that the very high exchange of methane was due to exchange reactions of methyl radicals, probably through the formation and decomposition of a quasi-molecule



They inferred an activation energy of about 5 Kcal. for this reaction. The present results are in agreement with this suggestion.

TABLE III
SUMMARY OF DEUTERIUM CONTENTS—DEUTERIUM BALANCE

Run No.	Substance	Deuterium content, mole %	Total H+D, mole-atoms	Total D, mole-atoms	Total deuterium content, mole-atom %
1	H ₂	28.6	52.8	15.2	
	CH ₄	23.3	134.8	31.4	
	C ₂ H ₆	4.8	195.0	9.4	
	C ₃ H ₈	17.2	27.2	4.7	
	C ₄ H ₁₀	16.6	40.0	6.6	
		Total	449.8	67.3	15.0
	Initial D ₂	100	68.2	68.2	
	Initial C ₂ H ₆	0	395.4	0	
		Total	463.6	68.2	14.7
2	H ₂	33.5	71.6	24.0	
	CH ₄	21.4	159.6	34.2	
	C ₂ H ₆	12.0	102.0	12.1	
	C ₃ H ₈	15.9	26.4	4.6	
	C ₄ H ₁₀	16.2	40.0	6.5	
		Total	399.6	81.0	20.2
	Initial D ₂	83.3	100	83.3	
	Initial C ₂ H ₆	0	300	0	
		Total	400	83.3	20.8
3	H ₂	68.0	118.8	80.8	
	CH ₄	34.1	62.4	21.3	
	C ₂ H ₆	11.4	129.0	14.7	
	C ₃ H ₈	23.5	13.6	4.0	
	C ₄ H ₁₀	21.2	18.0	3.8	
		Total	341.8	124.6	36.4
	Initial D ₂	89.6	129.4	116.0	
	Initial C ₂ H ₆	0	211.8	0	
		Total	341.2	116.0	34.0

Further, on the basis of Steacie and Phillips' mechanism, the formation of propane occurs solely by



and that of butane solely by



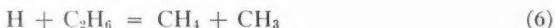
Also, the only reaction producing ethyl radicals in appreciable amount is



It would therefore be expected that propane would be deuterized in virtue of the rapid exchange of methyl radicals. However, butane would be expected to be entirely light. Actually, however, propane and butane are both exchanged to about the same extent. This relatively high exchange of butane is presumably to be ascribed to the exchange of ethyl radicals by a mechanism similar to that referred to above for methyl radicals, *viz.*,



In the previous paper it was pointed out that in order to account satisfactorily for the products of the reaction, it was necessary to assume that the reaction



was about four times as fast as



The only way to avoid such a requirement is to postulate some reaction, with a velocity comparable to that of (7), which consumes hydrogen and destroys ethyl radicals. The main possibilities are



However, if either of these reactions occurred rapidly, re-forming ethane from most of the ethyl radicals produced by Reaction (7), we would expect the residual ethane at the end of an experiment to be completely exchanged. Actually, the ethane is by no means largely exchanged, and we may therefore rule out the occurrence of Reaction (14) or (16) to an extent comparable with (7). Steacie and Phillips' conclusion that Reaction (6) is faster than (7) therefore receives additional support. The small amount of ethane deuteration which actually occurs is undoubtedly to be ascribed to the occurrence to some extent of the above reactions, and of Reaction (10)



Since the recombination reactions, (10) and (14), occur only to a comparatively small extent, the low quantum yield of the reaction (of the order of 0.1) cannot be ascribed to this cause. It is most likely due to inefficiency in the primary step.

References

1. BOLLAND, J. L. and MELVILLE, H. W. Trans. Faraday Soc. 33 : 1316-1329. 1937.
2. KNOWLTON, J. W. and ROSSINI, F. D. Bur. Standards J. Research, 19 : 605-612. 1937.
3. MELVILLE, H. W. and BOLLAND, J. L. Proc. Roy. Soc. London, A160 : 384-406. 1937.
4. MORIKAWA, K., BENEDICT, W. S., and TAYLOR, H. S. J. Chem. Phys. 5 : 212-225. 1937.
5. STEACIE, E. W. R. and PHILLIPS, N. W. F. J. Chem. Phys. 4 : 461-468. 1936.
6. STEACIE, E. W. R. and PHILLIPS, N. W. F. J. Chem. Phys. 6 : 179-187. 1938.
7. STEACIE, E. W. R. and PHILLIPS, N. W. F. Can. J. Research, B, 16 : 303-313. 1938.

EQUILIBRIA IN TWO-PHASE, GAS-LIQUID HYDROCARBON SYSTEMS

II. METHANE AND PENTANE¹

By E. H. BOOMER², C. A. JOHNSON³, AND A. G. A. PIERCEY⁴

Abstract

The densities and compositions of both phases in the *n*-pentane-methane solubility equilibrium have been determined at 25°, 55°, and 85° C. at total pressures from 35 to 190 atm. The critical pressures of complete miscibility were found. The properties of the system are discussed. Similar measurements at 25° C. and at pressures from 35 to 135 atm. were made on a system composed of a mixture of *n*-pentane and isopentane with methane.

Introduction

In the first paper (3) of this series the methods and apparatus required in the determination of the composition and properties of both phases in liquid-gas systems have been described. In this and subsequent papers the results obtained with a number of different hydrocarbon systems will be presented. A discussion of the results as a whole and the theoretical aspects of the subject will be reserved for a future report. In what follows, the results of measurements on two systems, *n*-pentane-methane and mixed-pentanes-methane, will be given.

Literature

The solubility of methane in *n*-pentane at 25° C. and at pressures as high as 100 atm. has been determined by Frolich *et al.* (5). The composition of the gas phase was not found. If solubilities are expressed as volume of gas at 25° C. and 1 atm. per volume of liquid, the results confirmed Henry's law at least for engineering purposes. The solubility of the gas did appear to increase somewhat more rapidly than the pressure, an effect that was found to be real and of considerable magnitude in the present work. The work of Hill and Lacey (6) on the solubility of methane in *n*-pentane and isopentane at 30° C. and one pressure, 20.4 atm., may be mentioned together with the more extensive work at three temperatures, 100°, 160° and 220° F. with *n*-pentane by Sage, Webster, and Lacey (9). A rapid increase in solubility of methane in pentane at high pressures and an approach to the critical pressure of complete miscibility is evident.

Materials

The preparation of the gas has been described (4). The composition of the particular sample used was: methane, 94.4; nitrogen, 5.6%. Traces of

¹ Manuscript received July 2, 1938.

Contribution from the Chemical Laboratories of the University of Alberta, Edmonton, Canada, with financial assistance from the National Research Council of Canada.

² Associate Professor of Chemistry, University of Alberta.

³ Research Assistant, Associate Committee on Gas Research, National Research Council, 1934-1936. Present address: 440 Massachusetts Ave., Boston, Mass., U.S.A.

⁴ University of Alberta Research Scholar, 1936-1937; Research Assistant, University of Alberta, 1937-1938. Present address: Turner Valley, Alberta.

other gases amounting to 0.1% may have been present. The pressure-volume-temperature behavior and density of this gas are shown in Table I. The data were obtained in the usual manner, one of the high pressure solubility pipettes and the gas measuring system described previously (3) being employed. If the data of Kvalnes and Gaddy (7) for pure methane are used as a standard, it may be stated that the gas used here approaches the ideal more closely than pure methane.

TABLE I
PRESSURE-VOLUME-DENSITY-TEMPERATURE BEHAVIOR OF THE GAS (94.4% OF
METHANE, 5.6% OF NITROGEN)

Pressure, atm.	Temperature, °C.	Density, gm./cc.	Deviation, PV/P_1V_1	Pressure, atm.	Temperature, °C.	Density, gm./cc.	Deviation, PV/P_1V_1
1.0	25.0	0.0007005	1.0	1.0	35.0	0.0006776	1.0
35.5		0.02684	0.9266	67.9		0.05118	0.8991
67.9		0.05344	0.8900	134.8		0.1067	0.8563
101.8		0.08318	0.8572	274.6		0.2042	0.9114
134.8		0.1133	0.8332	341.8		0.2343	0.9870
167.9		0.1423	0.8266				
201.4		0.1689	0.8375	1.0	55.3	0.0006358	1.0
208.5		0.1735	0.8422	67.9		0.04686	0.9211
243.6		0.1955	0.8726	134.8		0.09605	0.8902
274.6		0.2130	0.9031	243.6		0.1678	0.9226
308.5		0.2300	0.9397	308.5		0.2008	0.9774
341.8		0.2438	0.9822	369.6		0.2270	1.035
369.6		0.2541	1.019				
				1.0	60.4	0.0006262	1.0
				369.6		0.2232	1.036

A relatively complete list of the properties of the gas is given here for record only. This gas was used throughout most of this work and the relation between its properties and the results will be discussed in future reports.

The *n*-pentane was a commercial product obtained from petroleum. This pentane was washed with a nitrating mixture to remove traces of sulphur and aromatic compounds. It was then washed with dilute alkali solution, and with water, and was finally dried over calcium chloride and distilled through a fractionating column. The fraction retained and used had the following properties: boiling range (700 mm. of mercury), 35.7 to 36.0°C.; density (23°C.), 0.624; refractive index (22°C.), 1.3563.

A small amount of a mixture of isopentane and *n*-pentane was prepared by the fractional distillation of naphtha from Turner Valley, Alberta. The fraction showed the following properties: boiling range (700 mm. of mercury), 27.7 to 35.1°C.; density (23°C.), 0.620; refractive index (22°C.), 1.3539.

The fractionating column was reasonably efficient under high reflux and gave a good separation of the pentanes from other hydrocarbons. In the illustrative figures following, this mixture is designated as *i*-pentane.

Results and Discussion

The experimental results are shown in Tables II and III. Not all the results are included, approximately one-quarter having been discarded because of obvious errors due to leaks and failure to attain equilibrium. In the tables, S_1'' gives the solubility of methane in pentane as the mole ratio, and S_2' gives the pentane content of the gas phase as the mole ratio of pentane to total gas. Multiplying the first by 311 gives the solubility as cubic centimetres of methane at N.T.P. per gram of pentane. Dividing the second by 311 gives the number of grams of pentane per cubic centimetre of expanded gas at N.T.P. The mole fractions X , with subscripts 1 and 2 to designate methane and pentane and single primes and double primes to designate gas phase and liquid phase, are used to calculate the equilibrium constants.

TABLE II
METHANE-*n*-PENTANE SOLUBILITY EQUILIBRIUM

Pressure, atm.	Phase density, gm. per cc.		Phase composition, mole %						Equilibrium constant			
			Liquid			Gas						
	Liquid	Gas	C ₃ H ₈	CH ₄	N ₂	C ₃ H ₈	CH ₄	N ₂	S_1''	S_2'	X_2'/X_2	X_1'/X_1
35.5	0.590	0.0366	83.9	15.6	0.5	8.3	84.8	6.9				
	0.592	0.0352	83.6	16.1	0.3	8.3	88.4	3.3	0.189	0.0905	0.099	5.46
68.1	0.564	0.0630	69.8	29.8	0.4	5.1	88.0	6.9	0.427	0.0537	0.073	2.95
101.4	0.520	0.0984	56.7	42.1	1.2	4.7	88.9	6.4				
	0.518	0.0975	56.7	42.6	0.7	5.2	89.2	5.6	0.746	0.0521	0.087	2.10
134	0.481	0.146	45.0	53.6	1.4	5.8	87.4	6.8	1.190	0.0615	0.129	1.63
167.6	0.380	0.233	28.1	68.3	3.6	12.2	83.1	4.7				
	0.380	0.236	28.2	67.7	4.1	12.2	82.0	5.8	2.415	0.139	0.434	1.21
188	0.350	0.348	22.5	72.9	4.6	22.5	73.4	4.1	3.240	0.290	1.00	1.01

Temperature, 25° C.

35.5	0.563	0.0367	85.8	13.9	0.3	13.8	81.5	4.7	0.162	0.160	0.161	5.85
101.4	0.493	0.0972	60.3	38.6	1.1	8.1	86.2	5.7				
	0.495	0.0973	60.6	38.0	1.4	8.4	85.1	6.5	0.634	0.091	0.136	2.23
134	0.449	0.146	48.2	49.5	2.3	10.3	84.1	5.6	1.025	0.115	0.214	1.70
167.6	0.338	0.244	30.0	66.7	3.3	18.5	77.2	4.3				
	0.341	0.247	30.0	66.1	3.9	19.1	76.2	4.7	2.210	0.232	0.627	1.15
174.4	0.287	0.285	22.5	73.4	4.1	22.3	73.8	3.9	3.26	0.287	0.99	1.01

Temperature, 55° C.

35.5	0.563	0.0367	85.8	13.9	0.3	13.8	81.5	4.7	0.162	0.160	0.161	5.85
101.4	0.493	0.0972	60.3	38.6	1.1	8.1	86.2	5.7				
	0.495	0.0973	60.6	38.0	1.4	8.4	85.1	6.5	0.634	0.091	0.136	2.23
134	0.449	0.146	48.2	49.5	2.3	10.3	84.1	5.6	1.025	0.115	0.214	1.70
167.6	0.338	0.244	30.0	66.7	3.3	18.5	77.2	4.3				
	0.341	0.247	30.0	66.1	3.9	19.1	76.2	4.7	2.210	0.232	0.627	1.15
174.4	0.287	0.285	22.5	73.4	4.1	22.3	73.8	3.9	3.26	0.287	0.99	1.01

Temperature, 85° C.

35.5	0.532	0.0367	87.6	12.1	0.3	19.0	77.0	4.0	0.138	0.234	0.217	6.36
100.7	0.464	0.105	63.3	35.3	1.4	14.5	79.1	6.4	0.558	0.170	0.229	2.24
133.7	0.404	0.161	49.7	47.8	2.5	17.7	77.3	5.0				
	0.404	0.160	49.4	48.5	2.0	17.7	76.6	5.7	0.972	0.216	0.357	1.60
147.2	0.368	—	42.8	54.3	2.9							
	0.368	0.194	43.1	53.8	3.1	20.8	74.5	4.7				
	0.370	0.194	43.0	54.2	2.8	21.2	74.8	4.0	1.26	0.250	0.488	1.38
160.1	0.211	0.210	20.8	75.0	4.2	20.6	75.0	4.4	3.60	0.262	0.99	1.00

These constants, the reciprocal of the Ostwald absorption coefficient for methane, are common in the literature (10) as a means of describing liquid-gas equilibria.

TABLE III
METHANE-MIXED-PENTANES SOLUBILITY EQUILIBRIUM (TEMPERATURE, 25° C.)

Pressure, atm.	Phase density, gm. per cc.		Phase composition, mole %						Solubility		Equilibrium constant	
			Liquid			Gas						
	Liquid	Gas	C ₃ H ₁₂	CH ₄	N ₂	C ₆ H ₁₂	CH ₄	N ₂	S ₁ *	S ₂ *	X ₂ '/X ₂ "	X ₁ '/X ₁ "
34.4	0.585	0.0386	82.3	17.0	0.7	10.4	84.8	4.8	0.206	0.121	0.131	4.98
	—	0.0385	—	—	—	11.2	84.4	4.4				
66.6	0.554	0.0613	68.9	30.6	0.5	4.7	89.5	5.8	0.440	0.049	0.067	2.95
	0.556	0.0648	69.2	30.2	0.6	4.6	89.9	5.5				
100.3	0.512	0.100	55.6	43.2	1.2	4.4	89.8	5.8	0.757	0.045	0.076	2.06
	0.514	0.0971	57.2	42.2	0.6	4.2	88.0	7.8				
	—	0.1075	—	—	—	4.3	88.9	6.8				
133	0.440	0.1463	43.4	54.7	1.9	5.7	86.2	8.1	1.313	0.064	0.142	1.56
	0.445	0.1500	41.1	56.4	2.5	6.4	86.7	6.9				

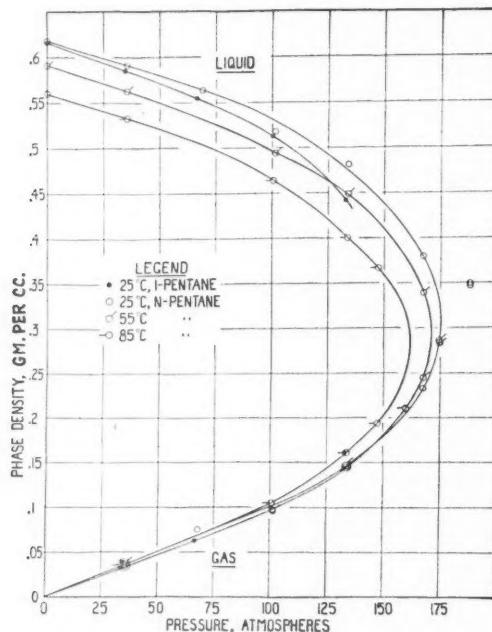


FIG. 1. Relation between densities of gas and liquid phases at constant temperature and pressure.

The results are shown in graphical form in Figs. 1 to 4. Figs. 1 and 2, showing respectively density and composition as functions of pressure at different temperatures, are fundamental in giving the directly measured quantities. Points in the single phase region for the *n*-pentane system are given in Table I at the highest pressure for each temperature. That these points are in the single phase region may be seen by reference to Figs. 1 and 2.

TABLE IV
CONDITIONS AT PRESSURE OF COMPLETE MISCELLIBILITY

Temperature, °C.	Pressure, atm.	Density, gm. per cc.	Pentane, mole %	S_1''	S_2'
25	175	0.307	19	4.02	0.234
55	171	0.293	25	2.91	0.333
85	162	0.285	31	2.75	0.450

n-Pentane

The properties of the system at the critical pressure of complete miscibility are given in Table IV. The data given in this table have been taken from enlarged copies of Figs. 1 and 2 and do not represent measured quantities.

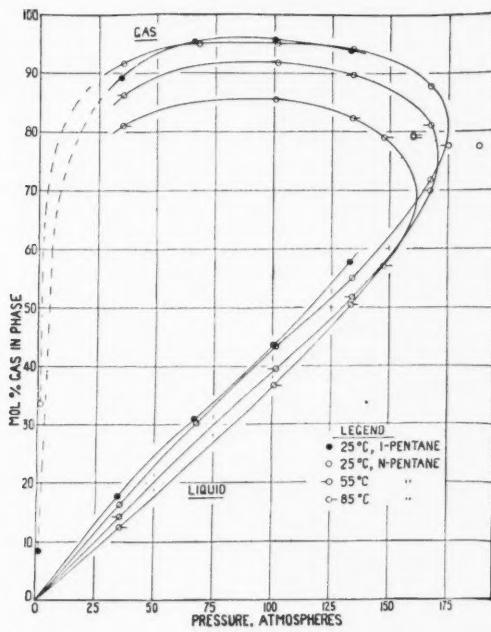


FIG. 2. Relation between composition of gas phase and that of the liquid phase at constant temperature and pressure.

The effects disclosed in Table IV are to be expected. With rising temperature, the critical pressure and density decrease, and the percentage of pentane in the system increases. Evidently the pressure of complete miscibility decreases more rapidly than the temperature increases and must approach the critical pressure of pentane.

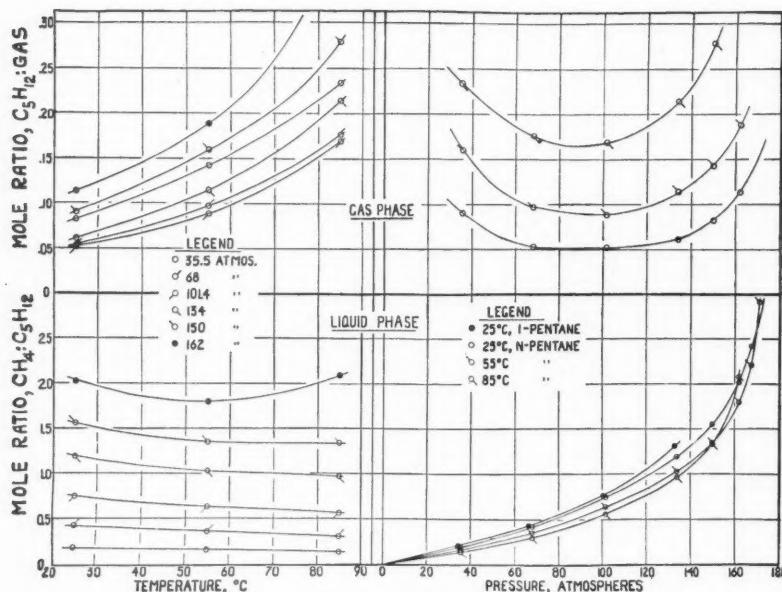


FIG. 3. Relation between solubilities, expressed as mole ratios of methane to pentane in liquid phase and pentane to gas in gas phase, and temperature and pressure.

The effect of increasing pressure of gas in the system upon the vapor pressure of pentane is shown in Fig. 2. Considerable vaporization of pentane into the gas phase occurs at relatively low pressures. The process becomes sufficiently important at 75 to 100 atm. to counteract the effect of increasing gas pressure, and the gas content of the gas phase reaches a maximum. The simple Poynting rule does not predict this maximum. In a future paper it will be shown that this maximum can be predicted, at least qualitatively. From the pressure corresponding to the minimum pentane-methane molecular ratio in the gas phase to the pressure of complete miscibility, under isothermal conditions, the concentration of pentane in the gas phase increases rapidly. The phenomenon may be described as one of increasing solubility of pentane in methane. The concentration of pentane in the gas phase is remarkably high and when expressed as partial vapor pressure, the ideal gas law being used, reaches meaningless values of several atmospheres.

The variation of the composition of the liquid phase is of interest in three particulars. At low pressures the gas content increases linearly with pressure. At pressures from 50 and 125 atm. there is a suggestion of concavity in the curves. (This effect has been found to be more pronounced in other systems, which will be discussed in subsequent papers.) It has been shown by Bassett and Dode (1) that with systems such as nitrogen-water, the liquid composition curves, plotted as in Fig. 2, go through a maximum and at no-

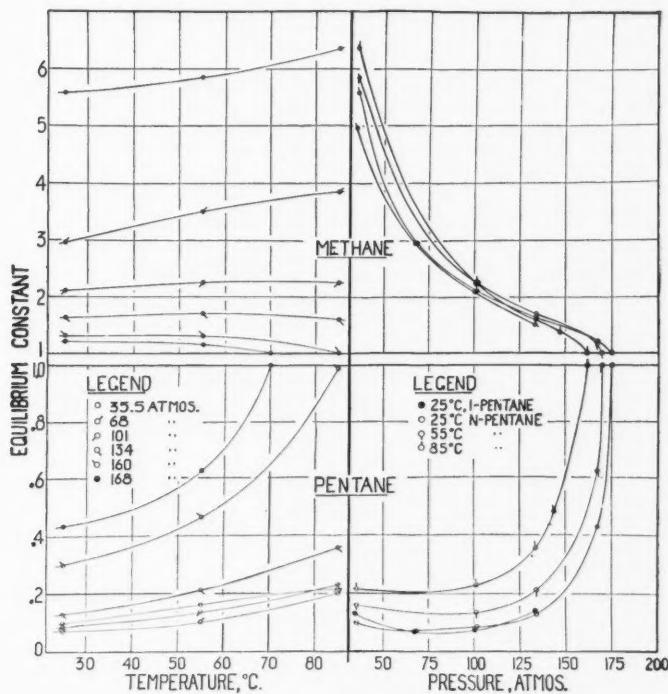


FIG. 4. Relation between equilibrium constants, the mole ratio of methane in gas phase to methane in liquid phase and similarly for pentane, and temperature and pressure.

pressure is there complete miscibility. In the present case, the great solubility of methane in pentane, compared to that of nitrogen in water, results in reversal of the trend of the curve and the existence of conditions of complete miscibility. Finally, at pressures below 150 atm. the effect of increasing temperature is to reduce the gas content of the liquid phase. In the region between 150 atm. and the critical pressures there is the phenomenon of retrograde gaseous solubility, the methane content of the liquid phase increasing with increasing temperature.

The work of Sage, Webster, and Lacey (9) on the *n*-pentane-methane system agrees very well with the present results. Their "bubble point" pressures and compositions may be compared with the present results by interpolation between the liquid phase data shown in Fig. 2. A regular small discrepancy exists, the methane content given by Sage, Webster, and Lacey being greater than that found here. The discrepancy may be attributed to the presence of nitrogen in the gas used in the present investigation.

The data of Fig. 2 have been expressed in a different manner, and this is shown graphically in Fig. 3. The solubility of methane in pentane (liquid phase) is shown as a function of temperature and pressure. The minimum in solubility of methane with increasing temperature is shown clearly at 162 atm. It is interesting also to notice that at the lowest pressure used, 35.5 atm., the effect of temperature on the solubility is least. The variation of solubility with pressure at constant temperature shows clearly the limitations of Henry's law. Evidently deviations become appreciable at 40 to 50 atm., and above 150 atm. the solubility increases very rapidly with pressure.

The effect of temperature and pressure on the solubility of pentane in the gas phase is shown more clearly in Fig. 3 than in Fig. 2. Under isobaric conditions, the pentane content of the gas phase increases with temperature, the increase being very great at high pressures. The minimum in pentane content with increasing pressure at constant temperature is shown very clearly. It is evident here, as in Fig. 2, that fixing the composition of the system and the temperature does not define the pressure except at the minimum point.

The use of equilibrium constants (10) to express and predict the behavior of gas-liquid systems makes their presentation here of some interest. Fig. 4 gives these constants for methane and for pentane as functions of temperature and pressure. In the range of conditions used, contrary to custom, it was not found necessary to use a semilogarithmic plot. Further, as found by Nederbragt (8), a semilogarithmic plot with temperature gave straight lines only at the lower pressures.

There is rough agreement between the equilibrium constants given here and those plotted by Souders, Selheimer, and Brown (10). The discrepancy is sufficiently great to make the use of their curves inadvisable except for approximate estimations. It does not appear that the equilibrium constants of one constituent are independent of the other constituent.

Isopentane

The few measurements on the mixed-pentane-methane system are, for comparison with the *n*-pentane system, shown in Table III and plotted in Figs. 1-4. Generally the differences between the two systems may be predicted on the basis that isopentane is more like methane in constitution than is *n*-pentane. Methane is definitely more soluble in the mixture of pentanes than in pentane alone. This has also been reported for isopentane at one pressure by Hill and Lacey (6). It is evident from Fig. 2 that the pressure of complete miscibility for the mixed pentanes and methane will be less than that for *n*-pentane and methane.

The equilibrium constant for methane in the mixed pentane system is slightly lower at all pressures used. This is due to the greater solubility of methane in isopentane and the slight difference in composition of the two gaseous phases. The equilibrium constants of the mixed pentanes have little meaning because the liquid is a mixture. They are shown, however, in Fig. 4 and it is evident that they differ barely by a significant amount from the equilibrium constant for *n*-pentane. The effect of isomerization of the solvent on the equilibrium constant of the solute is appreciable, but the equilibrium constants of the isomeric solvents are very nearly equal.

References

1. BASSETT, J. and DODE, M. Compt. rend. 203 : 775-777. 1936.
2. BOOMER, E. H. and JOHNSON, C. A. Can. J. Research, B, 15 : 363-366. 1937.
3. BOOMER, E. H., JOHNSON, C. A., and ARGUE, G. H. Can. J. Research, B, 15 : 367-374. 1937.
4. BOOMER, E. H., JOHNSON, C. A., and THOMAS, V. Can. J. Research, B, 15 : 360-362. 1937.
5. FROLICH, P. K., TAUCH, E. J., HOGAN, J. J., and PEER, A. A. Ind. Eng. Chem. 23 : 548-550. 1931.
6. HILL, E. S. and LACEY, W. N. Ind. Eng. Chem. 26 : 1324-1327. 1934.
7. KVALNES, H. M. and GADDY, V. L. J. Am. Chem. Soc. 53 : 394-399. 1931.
8. NEDERBRAGT, G. W. Ind. Eng. Chem. 30 : 587-588. 1938.
9. SAGE, B. H., WEBSTER, D. C. and LACEY, W. N. Ind. Eng. Chem. 28 : 1045-1047. 1936.
10. SOUDERS, M., SELHEIMER, C. W., and BROWN, G. Ind. Eng. Chem. 24 : 517-519. 1932.

EQUILIBRIA IN TWO-PHASE, GAS-LIQUID HYDROCARBON SYSTEMS

III. METHANE AND HEXANE¹

BY E. H. BOOMER² AND C. A. JOHNSON³

Abstract

The densities and compositions of both phases in the *n*-hexane-methane solubility equilibrium have been determined at 25°, 55°, and 85° C., at total pressures from 35 to 230 atm. The critical pressures of complete miscibility were found. The properties of the system are discussed. Similar measurements were made on a system consisting of a liquid mixture, principally isomeric hexanes, and methane.

Introduction

In previous papers, methods and apparatus for the study of equilibria in two-phase, gas-liquid, hydrocarbon systems were described (1), and the results of the investigation of the pentane-methane solubility equilibrium were presented (2). The present paper gives results obtained with the next higher paraffin hydrocarbon, hexane, and the same gas. It is hoped that in a following paper reporting on results obtained with a third hydrocarbon, heptane, the relations between the three systems will be discussed.

Literature

Measurements of the type to be described are relatively rare. Frolich *et al.* (3) have measured the solubility of methane in *n*-hexane at 25° C. and at pressures as high as 90 atm. In this pressure range they found that the solubility followed Henry's law fairly closely. The agreement was better when the gas pressure was corrected to the ideal state. However, the solubility of the gas increased somewhat more rapidly than the pressure. The same phenomenon was found in the present work, the magnitude of the effect increasing greatly at higher pressures. Hill and Lacey (4) determined the solubility of methane at one pressure, 20.4 atm., and one temperature, 30° C. Similar measurements showed that the solubilities of methane in *n*-pentane, isopentane, and *n*-hexane increased in that order. More extensive measurements on the hexane-methane system have been carried out by Sage, Webster, and Lacey at 100°, 160°, and 220° F. (8). They give the "bubble point" pressures, *i.e.*, the pressure at which a gas phase just forms, in three different liquid solutions. In the region in which comparison is possible, the present results are in substantial agreement with those of Sage, Webster, and Lacey.

¹ Manuscript received July 5, 1938.

Contribution from the Chemical Laboratories of the University of Alberta, Edmonton, Canada, with financial assistance from the National Research Council of Canada.

² Associate Professor of Chemistry, University of Alberta.

³ Research Assistant, Associate Committee on Gas Research, National Research Council, 1934-1936. Present address: 440 Massachusetts Ave., Boston, Mass.

Apparatus and Materials

The apparatus and experimental methods have been described (1).

The gas used was the same as that described previously (2); its composition was methane, 94.4; nitrogen, 5.6%.

Pure *n*-hexane was synthesized from *n*-propyl bromide according to the Wurtz reaction. *n*-Propyl alcohol was used as the original material. It was converted to *n*-propyl bromide in 80% yield by the hydrobromic-acid-sulphuric-acid method (7, p. 5). The directions of Lewis, Hendricks, and Yohe (6) for the similar synthesis of octane were followed, an anhydrous ether medium being used. The yield of *n*-hexane was not appreciable. It was found more satisfactory to carry out the reaction without the ether medium and to maintain careful temperature control. Briefly, the method was as follows: Anhydrous *n*-propyl bromide in a flask fitted with a reflux condenser was treated with a small portion of fresh, clean sodium wire. By means of a cooling bath the temperature was kept below 22° C. When reaction was complete, the sodium bromide was separated by filtration, and a second portion of sodium wire was added. This was repeated until the addition of sodium did not produce any reaction.

The liquid product was largely *n*-hexane containing some *n*-propyl bromide. It was fractionated carefully in an efficient vacuum jacketed, three foot column. The material retained and used as *n*-hexane had the following properties: boiling range (700 mm. of mercury), 68.8 to 69.1° C.; density (23° C.), 0.660 gm. per cc.; refractive index (21°), 1.3752.

A mixture, substantially isomeric hexanes, was prepared from naphtha from Turner Valley, Alberta. A five gallon lot was distilled through the column described and the fraction boiling at 60° to 70° C. retained. This material was treated exhaustively with a nitrating mixture, washed thoroughly with dilute alkali and water, and dried. Careful fractionation was carried out and a product having the following properties was retained: boiling range (700 mm. of mercury), 60.5 to 63.9° C.; density (20° C.), 0.664 gm. per cc.; refractive index (25° C.), 1.3739.

The properties suggest that the material consisted largely of β -methyl pentane and β -ethyl butane. The distillation curve shows that very little *n*-hexane was present.

Results and Discussion

The experimental results obtained with the *n*-hexane system are shown in Table I, and those with the mixed hexanes system in Table II. In the tables, S_1'' gives the solubility of methane in hexane as the mole ratio in the liquid phase, and S_2' gives the hexane content of the gas phase as the mole ratio of hexane to total gas. The quantity, 260.3 S_1'' , gives the solubility of methane in hexane in cubic centimetres at N.T.P. per gram. The quantity, $S_1''/260.3$, gives the vapor content of the gas phase in grams of hexane per cubic centimetre of gas expanded to N.T.P. The mole fractions, X , with subscripts 1 and 2 to designate methane and hexane, and single prime and

double primes to designate gas phase and liquid phase, are used to calculate the equilibrium constants given in the last two columns of the tables.

The results are shown in graphical form in Figs. 1 to 4. Figs. 1 and 2, showing density and composition as functions of pressure, are taken directly from the tables. Figs. 3 and 4, showing solubilities and equilibrium constants, include data from the tables and some data calculated from an enlarged copy of Fig. 2.

TABLE I
PROPERTIES OF THE *n*-HEXANE-METHANE SOLUBILITY EQUILIBRIUM

Pressure, atm.	Phase density, gm. per cc.		Phase composition, mole %						Solubility	Equilibrium constant	
			Liquid			Gas					
	Liquid	Gas	C ₆ H ₁₄	CH ₄	N ₂	C ₆ H ₁₄	CH ₄	N ₂	S ₁ ''	S ₂ ''	X ₂ ''/X ₂ ''

Temperature, 25° C.

1	0.655	—	—	—	—	19.6	80.4	—	—	—	—	—
36.2	0.635	0.0313	83.9	15.9	0.2	3.3	89.7	7.0				
	0.633	0.0292	83.5	16.2	0.3	2.6	92.0	5.4	0.192	0.0302	0.0350	5.66
68.4	0.609	0.0584	71.3	27.8	0.9	1.8	93.4	4.8	0.389	0.0188	0.0258	3.36
101.7	0.580	0.0909	59.6	39.2	1.2	2.1	90.9	7.0				
	0.579	0.0905	59.7	39.0	1.3	2.1	91.6	6.3	0.655	0.0204	0.0349	2.33
134.7	0.548	0.130	49.4	48.5	2.1	3.0	88.8	8.2	0.983	0.0305	0.0600	1.83
167.9	0.509	0.177	39.2	57.8	3.0	4.6	88.3	7.1				
	0.505	0.178	39.0	58.3	2.7	4.7	89.6	5.7	1.485	0.0488	0.1192	1.53
202.0	0.436	0.249	27.9	69.0	3.1	8.1	84.4	7.5				
	0.438	0.252	27.4	68.9	3.7	8.2	83.8	8.0	2.490	0.0888	0.2945	1.22
208.2	0.408	0.281	23.7	73.4	2.9	10.5	83.8	5.7				
	0.410	0.281	23.6	72.6	3.8	10.4	83.3	6.3	3.08	0.1168	0.442	1.145
229.3	0.371	0.367	18.0	77.1	4.9	17.5	77.9	4.6	4.27	0.212	0.968	1.01

Temperature, 55° C.

1	0.627	—	—	—	—	63.15	36.85	—	—	—	—	—
36.2	0.609	0.0297	85.5	14.2	0.3	4.9	87.3	7.8	0.166	0.0518	0.0576	6.14
101.7	0.556	0.084	62.8	35.5	1.7	3.4	89.9	6.7	0.565	0.0351	0.0540	2.53
167.9	0.484	0.163	42.1	55.3	2.6	5.7	88.2	6.0	1.315	0.0607	0.136	1.595
202.0	0.416	0.240	30.3	66.2	3.5	10.9	82.7	6.4				
	0.419	0.238	30.6	65.4	4.0	10.9	82.8	6.3	2.16	0.1225	0.369	1.257
208.2	0.373	0.277	24.9	71.0	4.1	14.6	80.8	4.6				
	0.373	0.275	25.0	71.5	3.5	14.5	80.8	4.7	2.86	0.170	0.583	1.133
219.1	0.319	0.323	18.9	76.8	4.3	18.6	76.8	4.6	4.06	0.229	0.986	1.00

Temperature, 85° C.

1	0.597	—	—	—	—	—	—	—	—	—	—	—
35.5	0.580	0.0301	87.1	12.6	0.3	11.3	82.9	5.8	0.145	0.1272	0.1296	6.56
101.4	0.530	0.0835	65.1	33.3	1.6	6.0	89.3	4.7	0.512	0.0641	0.0925	2.68
167.6	0.451	0.163	44.3	53.7	2.0	9.8	85.0	5.2	1.212	0.1088	0.2215	1.582
187.9	0.414	0.211	35.2	61.1	3.7	13.9	80.1	6.0				
	0.410	0.211	36.4	60.3	3.3	13.5	80.7	5.8	1.697	0.1588	0.383	1.33
201.0	0.324	0.321	25.0	71.4	3.6	25.0	70.3	4.7	2.85	0.334	1.00	0.985

TABLE II
PROPERTIES OF THE MIXED-HEXANES-METHANE SOLUBILITY EQUILIBRIUM
TEMPERATURE, 25° C.

Pressure, atm.	Phase density, gm. per cc.	Phase composition, mole %						Solubility	Equilibrium constant				
		Liquid			Gas								
		Liquid	Gas	C ₆ H ₁₄	CH ₄	N ₂	C ₆ H ₁₄	CH ₄	N ₂	S _{1''}	S _{2'}	X _{2'} /X _{2''}	X _{1'} /X _{1''}
1 35.5	0.659												
	0.629	0.0306	84.1	15.6	0.3		4.1	89.0	6.9				
	0.631	0.0294	83.8	16.1	0.1		3.6	92.7	3.7	0.190	0.0401	0.0460	5.70
101.4	0.571	0.0892	59.1	39.8	1.1		2.0	91.4	6.6	0.674	0.020	0.0332	2.29
167.6	0.497	0.182	38.0	58.5	3.5		4.6	89.3	6.1	1.54	0.0476	0.1195	1.525
201.0	0.386	0.291	23.2	73.2	3.6		12.0	82.8	5.2				
	0.391	0.287	22.5	73.8	3.7		11.8	82.8	5.4	3.21	0.135	0.522	1.125
215.0	0.399	0.395	22.2	74.3	3.5		22.3	72.9	4.8	3.35	0.287	1.01	0.982

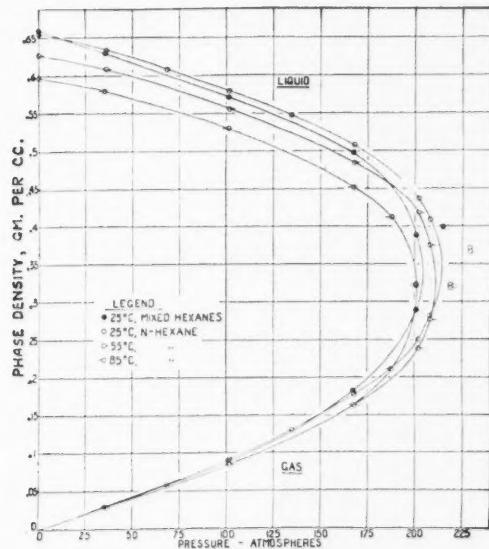


FIG. 1. Relation between densities of gas and liquid phases and pressure at constant temperature.

n-Hexane

At the lowest pressure used, 36 atm., methane dissolves to a greater extent in *n*-hexane than in *n*-pentane. This is in agreement with Hill and Lacey's (4) result at 20.4 atm. At higher pressures, however, methane is always more

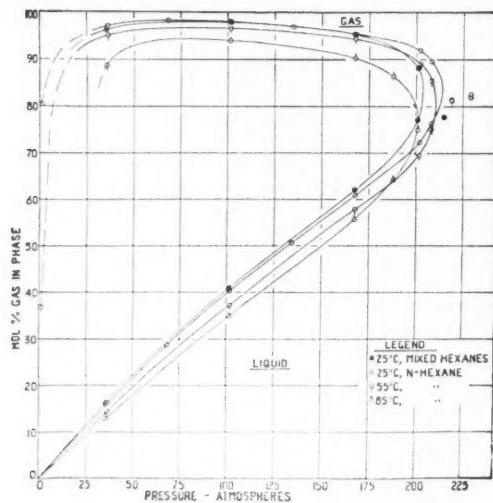


FIG. 2. Relation between composition of gas phase and that of the liquid phase and pressure at constant temperature.

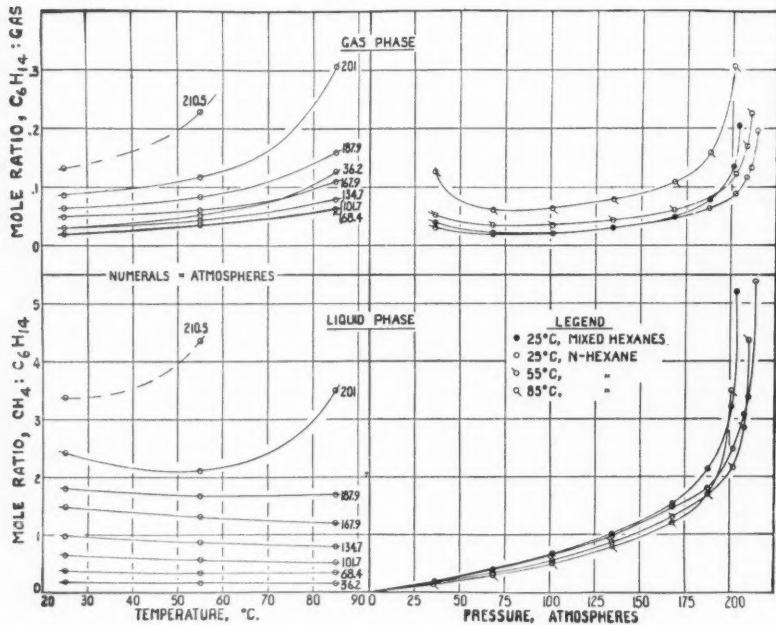


FIG. 3. Relation between solubilities, expressed as mole ratios of methane to hexane in liquid phase and hexane to gas in gas phase, and temperature and pressure.

soluble in *n*-pentane than in *n*-hexane. If solubility is expressed in cubic centimetres per gram, methane is more soluble in pentane than in hexane at all pressures up to the critical pressure for the pentane system. However, at pressures near the critical the solubility of methane in hexane is greater than it is in pentane at the corresponding pressure. This is only to be expected when the relative volatility of the two liquids is considered. The

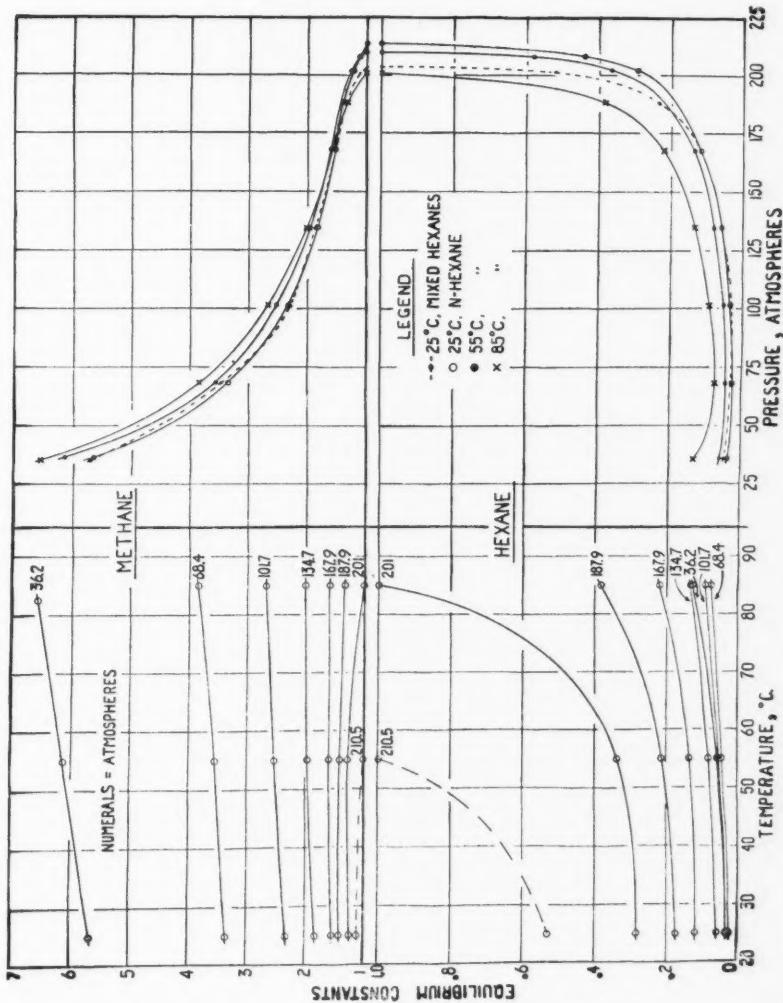


Fig. 4. Relation between equilibrium constants, the mole ratio of methane in gas phase to methane in liquid phase and similarly for hexane, and temperature and pressure.

pressure at which the vapor content of the gas phase is a minimum is about the same, 100 atm., in the two systems.

The agreement between the present results for the liquid phase and those of Sage, Websfer, and Lacey is good, except at the highest pressures used by them, 165 to 170 atm. The agreement between these solubilities and those found by Frolich is excellent. A small regular difference exists, the present figures being the smaller; this may be attributed to the nitrogen content of the gas.

The limitations of Henry's law are shown clearly in Fig. 3. Deviations become appreciable at 40 to 50 atm. and a rapid increase in solubility with pressure becomes marked at pressures greater than 100 atm. The upper limit of the pressure in Frolich's work was 90 atm.

When the pentane and hexane systems are considered as a whole, it is seen that their behavior is essentially the same. The differences that exist are in the direction expected on the basis that hexane is denser and less volatile than pentane. For example, the hexane system shows a higher pressure of complete miscibility. Again, the pressure at which a solubility minimum becomes evident in the temperature range used is about 200 atm. for hexane and 160 atm. for pentane. The curve of composition-pressure for the liquid phase, Fig. 2, is slightly concave to the pressure ordinate, the inflection leading to the critical region occurring at 150 to 175 atm. This effect is general (2) and more marked in the hexane system than in the pentane system.

The equilibrium constants, Fig. 4, change with temperature and pressure in a manner to be expected. The constant for hexane decreases to a minimum and increases rapidly to unity with increasing pressure. This has been found generally true by other investigators (5, 9). The constants for hexane are always less than those for pentane, in both cases of course approaching unity at the critical pressure. This might be expected to be a general rule for paraffins. The equilibrium constants of methane in the hexane system are greater than they are in the pentane system. The difference is small, about 5%, at the lowest pressure, but it increases as the critical pressure is approached. Evidently, the assumption that the equilibrium constant (9) for methane does not vary with the composition of the liquid holds only at relatively low pressures, where Henry's law is obeyed. Both equilibrium constants increase slowly with increasing temperature at low pressures. At high pressures, near the point of complete miscibility, the constants for hexane increase rapidly, and those for methane decrease slowly, with increasing pressure.

The properties of the system at the pressure of complete miscibility are given in Table III. The data have been taken from enlarged copies of Fig. 2 and are not the result of direct measurement. The shift in composition with increasing temperature is approximately linear with respect to the temperature. This is not true with regard to the two properties, pressure of complete miscibility and density. The pressure decreases to a greater extent and the density to a smaller extent in the interval from 55° to 85° C. than they do in the interval from 25° to 55° C.

Mixed Hexanes

The properties of the mixed-hexanes-methane system are given in Table II and shown in Figs. 1 to 4. This system bears much the same relation to the *n*-hexane system that the mixed pentane system did to the *n*-pentane system (2). The methane content of the liquid phase and the hexane content of the gas phase are greater in the systems containing mixed hexanes. The pressure of complete miscibility is lower in the mixed hexanes systems, the lowering being equivalent to the effect of a 40° to 50° C. temperature rise. Such a result might be expected when branched and straight chain isomers are compared. A molecule of the branch chain isomer resembles the methane molecule more closely than does a molecule of the straight isomer. This resemblance is shown in the van der Waals forces, measured for example by freezing points or by internal pressure. These forces increase in the order, methane (relatively small), branch chain isomer, straight chain isomer, so that the difference between the first two molecules is less than the difference between the first and third molecules. The disturbance of intermolecular fields of force is less and consequently the mutual solubility is greater on mixing the former pair than is the case for the latter pair.

TABLE III
CONDITIONS AT PRESSURE OF COMPLETE MISCELLIBILITY

Temperature, °C.	Pressure, atm.	Density, gm. per cc.	Hexane, mole %	S_1''	S_2'
<i>Hexane</i>					
25	214	0.347	16.5	5.38	0.1975
55	210.5	0.325	19.7	4.36	0.246
85	201	0.310	23.5	3.50	0.307
<i>Mixed hexanes</i>					
25	203.5	0.340	17.0	5.21	0.205

References

1. BOOMER, E. H., JOHNSON, C. A., and ARGUE, G. H. Can. J. Research, B, 15 : 367-374. 1937.
2. BOOMER, E. H., JOHNSON, C. A., and PIERCEY, A. G. A. Can. J. Research, B, 16 : 319-327. 1938.
3. FROLICH, P. K., TAUCH, E. J., HOGAN, J. J., and PEER, A. A. Ind. Eng. Chem. 23 : 548-550. 1931.
4. HILL, E. S. and LACEY, W. N. Ind. Eng. Chem. 26 : 1324-1327. 1934.
5. KAY, W. B. Ind. Eng. Chem. 30 : 459-465. 1938.
6. LEWIS, H. F., HENDRICKS, R., and YOHE, G. R. J. Am. Chem. Soc. 50 : 1993-1998. 1928.
7. ORGANIC SYNTHESSES. Vol. I. John Wiley and Sons, New York. 1921.
8. SAGE, B. H., WEBSTER, D. C., and LACEY, W. N. Ind. Eng. Chem. 28 : 1045-1047. 1936.
9. SOUDERS, M., SELHEIMER, C. W., and BROWN, G. Ind. Eng. Chem. 24 : 517-519. 1932.

